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**Effect of the presence of a third phase on capillary pressure of
consolidated sandstone by the centrifuge method**

Toskey, Eric Douglas, M.S.

University of Alaska Fairbanks, 1990

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300 N. Zeeb Rd.
Ann Arbor, MI 48106

**EFFECT OF THE PRESENCE OF A THIRD PHASE
ON CAPILLARY PRESSURE OF CONSOLIDATED SANDSTONE
BY THE CENTRIFUGE METHOD**

**A
THESIS**

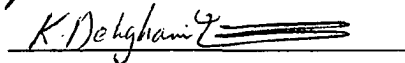
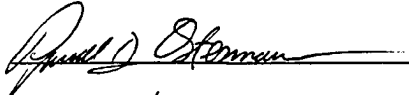
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MASTER OF SCIENCE

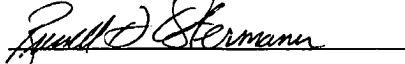
**By
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Fairbanks, Alaska
December, 1990**

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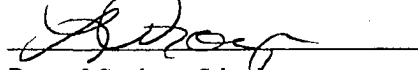


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Abstract

An experimental investigation has been made into two phase capillary pressure phenomena in porous media containing three immiscible fluid phases. Using the centrifuge method, drainage capillary pressure curves were generated for three phase systems and compared to those of two phase systems in a strongly water wet, consolidated, Berea sandstone. Results of the investigation show that a third trapped saturation of oil, gas, or water can affect the residual fluid saturation values, the shape of the capillary pressure curves, and the saturation distribution of the core. Furthermore, it was determined that the Hassler and Brunner method (for determining endpoint saturations in centrifuge experiments) is susceptible to erroneous results in three phase systems. Therefore, in any drainage or imbibition process, the effect of a third phase cannot be considered insignificant in determining the capillary pressure – saturation relationships between two fluids in a three phase system.

To my sister, Kim, and brothers, Pete and Mark,
that they never give up on their dreams or themselves.

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1. Introduction

Although it is well known that surface seeps of oil and natural gas existed several centuries ago, exploration for and the production of petroleum dates back little further than the end of the 19th century. In these early days of "wildcatting" and "gushers," little reservoir engineering was employed to produce the oil. Part of the reason for this was because so little was actually known about the nature of hydrocarbon reservoirs or the movement of the fluids therein. Besides possibly some subsurface maps generated by outcrop projections, samples of rock cuttings from the well, and maybe some production data, most early oil magnates had little information with which to forecast reservoir performance.

Since the 1930's, many technological advances and considerable efforts through research have greatly improved our understanding of hydrocarbon reservoirs and the mechanisms which control the drainage of their fluids. Earlier research was accomplished by extending the science of hydrology to petroleum reservoirs. Building on the basic concepts of multiphase fluid behavior in porous rocks, subsequent research efforts have broadened to cover nearly every imaginable aspect of petroleum production. Still, there are many questions which are in need of further research. Some of these questions involve fundamental concepts which have never been fully explained. One of these fundamental concepts which still deserves attention is the phenomenon of capillary pressure in porous rocks containing three phases of fluids.

Almost all reservoirs contain three fluid phases within their pore space sometime in their production history. The three phases include two immiscible liquid

phases, water and oil, and a gas phase. The water phase is typically either a connate brine, encroaching aquifer, or injected water from a waterflood or condensed steamflood. The oil phase is a multicomponent mixture of hydrocarbons in the liquid state. If the reservoir pressure is below its bubble point (the pressure at which solution gas begins to bubble out of the oil), then the oil exists in a pressure and temperature dependent equilibrium with free natural gas. The gas phase may also be an injected gas, like air, carbon dioxide, or super heated steam. As stated above, "normal" reservoirs will contain three fluid phases if the pressure is below bubble point pressure. In addition, reservoirs undergoing enhanced oil recovery (EOR) techniques generally involve the interaction between three separate phases. Examples of EOR methods are a steamflood, a CO₂ flood (miscible or immiscible), in-situ combustion of oil, and WAG (water – alternating – gas) slug injection process.

In any of the above recovery processes, each of the three phases may be mobile or static, depending upon their saturations (the percent of total pore volume occupied by the phase). In a three phase system there always exists at least one mobile phase. There also may be two mobile phases free to flow about one static phase or three phases flowing amongst each other.

The behavior of fluids in a reservoir can be described as a dynamic state wherein each fluid seeks to balance the forces against it. Reservoir fluids under pressure draw down are influenced by pressure forces, gravity forces, viscous forces, and surface forces (i.e., capillary pressure). It is impossible to say which forces acting on the fluid are the most important because the relative influence of each force is variable in relation to the others. Pressure and viscous forces are flow rate

dependent, dominating fluid behavior at high flow rates. Pressure forces, once they overcome gravity forces, work on the fluids to perpetuate fluid movement and cause continuous phase distributions. Capillary forces, on the other hand, act as a resistance to flow by retaining the fluids in the rock. Capillary forces tend to resist the segregation of the fluids caused by the gravity forces. Capillary forces work against the production of oil from porous media by retaining discontinuous small saturations of oil.

From this, it is easy to understand the importance of surfacial forces on fluid recovery. The fluid – fluid interfacial forces on a fluid are known as the interfacial tension. The rock – fluid forces are the wettability forces. Any fluid coexisting in a porous medium with another fluid will be influenced by both the interfacial tension and the wettability. The capillary pressure of a fluid – fluid interface in porous media is defined as the product of these two forces divided by the radius of curvature of the interface. Therefore, capillary pressure is dependent upon the surfacial forces of the rock and fluids and upon the pore size and shape. Capillary pressure is used as a measure of the ability of the rock to retain fluids in its pore space. Capillary pressure controls the mechanisms of fluid entrapment and microscopic displacement and determines static fluid distributions. At low flow rates, capillary pressure can influence macroscopic flow patterns.

The importance of obtaining accurate capillary pressure data is paramount to any accurate study of petroleum recovery from a reservoir. Capillary pressure data are often used as input in numerical reservoir simulators for the prediction of reservoir behavior. When two phases are present in the reservoir, capillary pressure data for the two phases is used as a physical description of the rock – fluid system.

When three phases are present, however, it has been common to substitute two phase capillary pressure data for three phase data. This has been done because little is known about how the presence of a third phase in the reservoir might affect the capillary pressure of the other two phases. In fact, little experimental data of three phase capillary pressures has been published in the petroleum literature.

The goal of this study is to measure capillary pressures between two fluids in the presence of an immobile third phase. The study also presents a theoretical background on capillary pressure in two and three phase systems and the factors which influence it. Measurements of capillary pressure for three phase systems has been discussed and some conclusions drawn concerning the applicability of using two phase capillary pressure data for three phase systems.

As an additional note, although capillary pressure is a two phase phenomenon, the capillarity of a three phase system is often referred to herein as "three phase capillary pressure." This misnomer is used simply for the sake of convenience so as not to further cloud its discussion. A more correct terminology for three phase capillary pressure is "two phase capillary pressure in the presence of a third phase."

2. Theory and Literature Review

2.1 Nature of Porous Media

A porous medium is any material which has interconnected void space within its pore structure. The percent of void space is called the rock porosity. The degree to which these voids are interconnected, forming pathways through which fluids can flow, is called the rock permeability. A material must have both a porosity and a distinct, measurable permeability to be called a porous medium. Many materials classify as porous media and the study of the physics of porous media has a wide variety of applications. Problems of fluid flow and static fluid distribution in porous media can be found in the use of ceramics, wood, or paper, the study of soils or the human lung, or the design of "breathable" clothing material. Since the focus of this thesis is on the behavior of fluids in consolidated sandstone, this section will discuss only consolidated sandstone as a porous medium. In fact, whenever the term, porous media, is used within this text, it will imply a porous consolidated sandstone.

Besides porosity and permeability, there are many properties of porous media which have relevance to the production of petroleum. A brief description of the physical properties of sandstones, as they relate to capillary pressure is given here. Dullien (1979) gives a much more detailed description of porous media, including porosity, permeability, pore size and shape (topology), pore size distribution, surface area, formation resistivity factor, and grain packing. He also discusses the heterogeneities and anisotropies of these properties as well as the methods used to measure them.

Sandstones are formed in the earth's subsurface by the compaction and cementation of clastic material, mostly sand grains, over a long period of time. Typically, sandstones contain quartz, feldspars, and various clay minerals with varying amounts of cement. The massive sandstone accumulations large enough to hold an economic reserve of petroleum are originally laid down in marine, alluvial, or eolian environments. It is rare to find a natural deposit of sand under these conditions which does not consist of other materials as well. Therefore, sandstones almost always contain clay or shale in the form of intergranular matrix or partially continuous lenses. The cement which bonds the grains together at their points of contact is usually formed by the deposition of minerals, like calcite, out of the formation waters percolating through the bed. The finished product is a porous structure of round to angular grains of sand, flat clay platelets, and matrix material mostly cemented by chemically bonded minerals.

Pore spaces or voids in between the grains can be filled with fluids like water, oil, or gas. These voids can comprise from 1 – 30 percent of the total bulk volume of the rock. Sandstone permeability is computed using Darcy's Law, named for the Frenchman, D'Arcy, who first measured water flow in a linear sand pack. Permeability can vary from very tight beds heavily laden with clays or shales to extremely permeable beds of clean eolian sand with minimal cementing material. The permeability is a function of pore (space) and pore throat size and shape, and the tortuosity of the intergranular channels. On a grand scale, the permeability of a reservoir is usually a directional property, influenced by geologic properties like bedding, sedimentary structures, sediment texture, fractures, faults, and impermeable lenses or intercalations. A good description of the geologic parameters

which affect petroleum production can be found in Pirson's reservoir engineering textbook (Pirson, 1958), or in Willhite's waterflooding monograph (Willhite, 1986), or in many recent publications on petroleum geology.

The surface area of the rock particles and matrix material is another important property of porous media. In a typical reservoir, 1 cubic inch of rock has more than 100 square feet of surface area exposed to a fraction of an ounce of fluid. Considering the fact that this surface area is comprised of a variety of minerals and clays distributed irregularly, it is easy to see that the surface phenomena of reservoir rock greatly influences petroleum recovery and the distribution of initial and residual fluid saturations. Indeed, the chemical interaction of the reservoir and injected fluids with the rock surface can be the controlling factor in determining petroleum recovery efficiencies. This interaction is discussed further in the next section, Rock and Fluid Surface Chemistry.

2.2 Rock and Fluid Surface Chemistry

2.2.1 Interfacial Tension

Wherever two fluids or a fluid and a solid come in contact with one another there exists an interface. There is associated with this interface a free energy or surface tension. The surface tension, an equivalent term for free surface energy, is the net result of the cohesive and adhesive forces at the surface and can be described as the work or energy required to extend the interface (Adamson, 1976). In order for a two phase interface (solid - liquid, solid - gas, liquid - gas, or

immiscible liquid – liquid) to be considered stable, the free energy must be positive. In other words, a positive amount of work must be put into the system to stretch the interface beyond its equilibrium position. If the free surface energy is negative, the surface is unstable and will do work by extending or contracting the interface spontaneously. This can be visualized as two phases instantaneously contacting one another. Initially, the free energy may be negative, causing the interface to expand like a drop of water flattening against a glass surface or contract like water in air quickly forming a spherical drop.

In the above examples, the contraction or expansion at the interface is caused by movement of the surface molecules to the interior of the drop or the interior molecules to the exterior of the drop, respectively. According to Adamson (1976), the modern pioneer of surface chemistry, most of the free energy is developed within a few molecules of the surface. This implies that molecular movement also is restricted to the outermost molecules. For the water spread on a glass surface, the adhesive force of the glass surface molecules acting on the neighboring water surface molecules is greater than the cohesive force of the interior water molecules. As the interior molecules, previously at equilibrium with each other, move into the interface to lower their potential energy, the preexisting surface molecules are forced outward, extending the surface. For the water droplet surrounded by air, the water surface molecules experience a stronger cohesive force to their neighboring water molecules than to their neighboring air molecules. The net effect is a “pulling in” of the surface molecules to the interior and the water droplet contracts to a sphere.

As these examples show, the relative mobility of gas and liquid molecules means that fluid – fluid interfaces can and usually do possess a curvature about

them, whereas fluid – solid interfaces do not. An early observation by nineteenth century physicist Plateau (1873) showed the sum of the inverses of the two radii which uniquely describe liquid drop curvature is always constant. This requires a liquid drop surface to contract to a state of minimum surface area per volume; hence, a sphere. For gas – liquid or high tension liquid – liquid systems, this is the case. For low tension immiscible liquids, however, the interfacial tension may not be sufficient to cause a high degree of curvature and the fluids may have flatter interfaces.

The spreading or contracting (“beading”) of a fluid on a surface in the presence of another fluid is controlled by the interfacial tensions. The preferential spreading of a fluid on a solid surface is called the wettability of the solid and is deferred to a separate section in order to give it broader treatment. The conditions for the spreading of a fluid on the surface of a second fluid and in the presence of a third fluid are outlined below.

In porous media, fluid distribution can vary from bubbles and droplets, to multipore globules, to continuous channel flows and films. In water wet consolidated sandstone, oil frequently exists as a film of variable thickness between water and gas. This is primarily due to the fact that gas-water interfacial tension is greater than the sum of the oil-water and oil-gas interfacial tensions (Adamson, 1976). The condition of oil spreading on a water surface is based on this inequality and is quantitatively determined by the spreading coefficient,

$$S_{o/w} = \sigma'_{wg} - \sigma_{og} - \sigma_{ow}$$

where $S_{o/w}$ is the final spreading coefficient of oil over water and σ_{wg} , σ_{og} , and σ_{ow} are the interfacial tensions. The prime over the σ'_{wg} designates the interfacial

tension between water and gas when the water is covered with a ("Gibbs") monolayer of oil. The value of σ'_{wg} is generally less than the normal σ_{wg} . This equation corresponds to the thermodynamic equilibrium of all three fluids. When $S_{o/w}$ is positive spontaneous spreading of oil over water will occur. If $S_{o/w}$ is near zero or negative, then no spreading will occur and oil will sit as a lens on top of the water.

Residual fluid saturations and their distributions are strongly dependent upon the value of the spreading coefficient and the rock wettability (Chatzis, et al., 1988). The mechanisms which trap fluids in water wet media is discussed in section 2.3.2.

Since petroleum bearing sandstone contains two, if not three, phases of fluids, the chemical interaction of these fluids with themselves and with the rock is an important factor in determining the residual fluid saturations. Many investigators have concluded that a reduction in interfacial tension can improve recovery. In both oil wet and water wet porous media (Wagner and Leach, 1966) and even in water wet porous media with wettability reversing rigid films formed on the surface (Reisberg and Doscher, 1956), interfacial tension reduction can increase displacement efficiencies. Indeed, the real significance of understanding surface or interfacial tension is born in its control over many fluid flow and distribution governing parameters such as capillary pressure, relative permeability, and, most importantly, wettability. The effects of interfacial tension on wettability and capillary pressure are outlined in their respective sections. The following section (Section 2.2.2) briefly discusses wettability. Capillary pressure is addressed in sections 2.3.1 (two phase) and 2.4.1 (three phase). Because this literature review is

concerned with the static and quasi-static behavior of fluids, dynamic phenomena such as relative permeabilities will not be addressed.

2.2.2 Wettability

This section presents the concept of petroleum reservoir rock wettability and discusses how it may be affected or changed. The effect of wettability on capillary pressure will be addressed in the discussion of two phase capillary pressure.

The term wettability is not specific to the science of petroleum recovery but is applied in many different fields of study. Since the early part of this century petroleum engineers and scientists have increasingly recognized its importance in maximizing oil recovery and the definition of wettability has evolved, if you will, from a simple measure of contact angle to a complex study of several interdependent reservoir rock and fluid properties.

It is easiest to define wettability not from the approach of early investigators, but by presenting the more recent concepts of wettability. This is due to the fact that for a large period of petroleum production history (until 1969) wettability was a somewhat vague and intangible subject. In fact, wettability was not considered an absolute property of the rock. Discussions of wettability were always made in reference to relative wettability. There lacked a good method for quantitative wettability measurement of actual reservoir cores using reservoir fluids. It was difficult to correlate simultaneous investigations into wetting phenomena, and results frequently contradicted one another. There was even disagreement over the relative advantages of the wetting states.

In 1969, Donaldson, Thomas, and Lorenz developed a method to measure reservoir wettability quickly and easily on the centrifuge. Their method, known as the USBM method, was derived from many well established observations that had been circulating about the literature for some time. The theoretical basis for the USBM method was first established twelve years earlier by Gatenby and Marsden. They stated that rock wettability is a function of the work required to move a stable fluid interface within a pore. This work is directly related to the areas under and above the positive and negative capillary pressure curves. The positive capillary pressure curve is a measure of the positive work required by the system to move the interface. This occurs during the drainage process whereby non-wetting fluid, with the aid of externally applied work, drains the wetting fluid from the rock. The negative capillary pressure curve is a measure of the work done in forcing the process of imbibition. Imbibition is the displacement of non-wetting phase by wetting phase. The initial drainage or imbibition of wetting phase is characteristically different than subsequent drainages or imbibitions. As a matter of nomenclature, the initial drainage or imbibition is called the primary drainage or imbibition. Subsequent drainages or imbibitions are called secondary, tertiary, quaternary, etc.

The USBM method defined a wettability index, W , which is the logarithm of the ratio of the area under the secondary drainage curve, A_1 , over the area under the primary, negative imbibition curve, A_2 .

$$W = \log (A_1/A_2)$$

The value W provides both a numerical magnitude of wettability as well as a qualitative index. For water wet cores, W is positive; whereas for oil wet cores, W is negative.

The most widely accepted method prior to 1969 was that of Amott (Anderson, 1986). Like the USBM method, the Amott (1959) test calculated a qualitative wettability index and was similarly based on the ratio of drainage characteristics to imbibition characteristics. Other qualitative measurement methods based on the early theories on wettability include the use of relative permeability data (Coley et al., 1956; Jennings, 1957), imbibition (Killins et al. 1953), displacement pressure (Benner et al., 1942), and capillary pressure (Gatenby and Marsden, 1957; Johansen and Dunning, 1959). These theories are mentioned because, as subsequent research efforts have shown, wettability does influence relative permeability, capillary pressure, minimum displacement and threshold pressures, and free imbibition rates, as well as fluid distributions and the mechanisms of residual fluid entrapment and recovery. Publications supporting these relationships are too numerous to refer to in their entirety. Some are discussed in later sections of the text. Methods employing nuclear magnetic relaxation (Brown and Fatt, 1956) and methylene blue dye adsorption (Holbrook and Bernard, 1958) also exist as quantitative measures of wettability but have never been widely accepted (Donaldson, et al., 1969).

In determining the wettability of a solid surface, the relative magnitudes of the fluid-fluid and rock-fluid surface tensions play a major role. Because of the low molecular density of gases, gas-liquid interfaces have a higher interfacial tension than liquid-liquid interfaces. Similarly, gas-solid surface tension is usually higher than liquid-solid surface tension. In general, for clean solid surfaces, the fluid with the lowest surface tension will preferentially wet the solid. In a glass container partially filled with water, water will rise on the wall above the air-water surface due to the lower surface tension between glass and water than between glass and

air. In a similar teflon container holding water and oil, the oil-teflon surface tension is lower than that of air or water, and the oil will preferentially wet the teflon at both interfaces. It would be said from this example that the glass surface is "water wet" and the teflon is "oil wet".

It is possible to adjust the wettability of the reservoir. Early researchers learned to control the wettability by injecting oil soluble or water soluble compounds which would adsorb on the rock surface (Bobek et al., 1958). Recently, adhesion of crude oil to the surfaces was expressed as the key to wettability alteration (Morrow, et al., 1986). Wettability alteration, they discovered, occurs by the deposition of a tenacious film, like a monolayer of asphaltenes. The formation of oil wet surfaces is caused by the chemisorption of basic polar compounds to acidic silica surfaces (Benner and Bartell, 1941). These basic compounds are polar surfactants found in the crude oil (Donaldson et al., 1969; Benner and Bartell, 1941; Johansen and Dunning, 1959; Morrow, et al., 1986). Oil wet cores are strongly influenced by pH. Injected sodium hydroxide or surfactant adsorbed on the rock surface has been shown to significantly increase the water wetness and improve recovery (Mungan, 1966; Brown and Neustadter, 1980). For some oil wet rocks, water wettability enhancement may decrease recovery if the resulting wettability becomes intermediate wet (Mungan, 1964).

Besides the surface chemistry of the sandstone and reservoir fluids, other parameters have been found to affect wettability, but to a much lesser extent. By measuring contact angles of pure and crude oils on a silica surface, Brown and Neustadter (1980) concluded the wettability could be strongly modified by the surface texture, was dependent on the displacement process kinetics, and for weakly water wet surfaces, the wettability changed with the saturation history.

Sandstone wettability is dependent upon the unique surface properties of each rock component (i.e. silica, clays, carbonates, heavy oil deposits) as well as the magnitude and continuity of their distribution (Craig, 1971). Clean sandstone (free of organic matter) is mostly quartz and is strongly water wet because of the polarity of the silica in the quartz. However, most reservoir sandstones contain considerable amounts of clays and portions of reservoir with highly polar compounds adsorbed from the oil onto the rock surface. Such adsorption can significantly affect the surface tensions by changing the surface chemistry of the rock's interstices. Because reservoir rock wettability is a strong function of surface tension, wettability is dictated by the characteristics of the porous media and the fluids which it contains.

There are two other theories on wettability which differ from that previously defined and deserve mention. Although wettability is most often considered a continuous, but non-constant, property of the rock surface, it has been proposed to occur as a discontinuous or directionally dependent continuous property. Porous media with "mixed wettability" can be visualized as a network of continuous water saturated, water wet channels through small pores, around grain contact points, and in pore throat. The water separates and isolates large oil containing pores with surfaces made strongly oil wet by crude oil surfactant adsorption. Mixed wettability rocks can result in improved recoveries by causing a shift in the oil permeability curve to higher water saturations. For mixed wettability reservoirs under a slow gravity drainage, trapped oil can be produced by surface film drainage to very low residual saturations, depending on the rock characteristics and fluid properties (Salathiel, 1973). The concept of mixed wettability implies directional continuity because the oil can flow through the large oil wet pore channels.

In a fractionally wet porous medium, pore surfaces are either oil wet or water wet and the degree of fractional wettability is directly proportional to the percentage of oil wet surface area. This idea was originally proposed as an improved model for reservoir wettability over the industry standard smooth surface contact angle (Brown and Fatt, 1956). Since rock surfaces consist of many different minerals, each with its own surface chemistry and capacity to adsorb surface active materials, it was believed that the concept of fractional wettability better represented these heterogeneities than the single-valued contact angle. Because it does not adversely affect the capillary pressure function, the fractional wettability model is theoretically valid (Fatt and Klikoff, 1959). However, it is not applied to most reservoir rocks.

The importance of wettability is extant in all methods of petroleum recovery. In secondary recovery, wettability is especially important as it has major influence on the residual oil saturation and its distribution (Bobek et al., 1958). In general, the greater the water wetness of a sandstone, the less likely oil will be trapped in the highly retentive smaller pores. Experiments by Melrose and Brandner (1974) showed a decrease in water wetness from 0° - 45° contact angle doubled the capillary forces resisting the displacement of residual oil ganglion. They concluded complete water wetness is optimal as oil is contained in the larger more permeable pores. A recent study, however, has reported that oil recovery may actually be improved by decreasing the water wetness to a weakly water wet state which can reduce water permeability and improve the flow of oil in pore bodies (Morrow et al, 1986). Their results violate the accepted theory of wettability which implies water permeability is reduced by increasing water wettability. In most sandstones, strong water wettability is optimal to maximize the recovery efficiency.

2.3 Two Phase Fluid Behavior in Porous Media

2.3.1 Capillary Pressure

2.3.1.1 Definition

The following is a brief, but broad, description of capillary pressure and its relation to porous media. There are many publications which provide a good treatment of capillary pressure; however, Gibbs (1961), Dullien (1979), and Morrow (1970) are especially worth noting.

Because of the interfacial forces between two immiscible fluids, there exists a pressure difference between them. The pressure difference across the interface is called capillary pressure and is defined as the non-wetting phase pressure minus the wetting phase pressure, $P_c = P_{nw} - P_w$. The early advances in the science of capillarity in porous media were made by soil scientists and hydrologists (Haines, 1927; Hackett and Strellan, 1928; Haines, 1930; Smith, et al., 1931; Smith, 1933). Their work, and others', laid the foundation for the study of capillarity in petroleum reservoir rocks. Understanding capillarity in petroleum reservoir rocks is a much more difficult task than in soils as the number of fluid phases increases from one to three, the fluid and rock surface chemistry is dramatically more complex, and it is nearly impossible to "imitate" exactly fluid flow in a reservoir several thousand feet below the earth's surface. A truly landmark publication of the observation of capillary pressure properties of porous media is M.C. Leverett's (1941) "Capillary Behavior in Porous Solids". In air-water experiments, he showed the relationship

between capillary rise and water saturation. Many of his discoveries and ideas are now considered "general knowledge" amongst petroleum researchers.

Capillary pressure is a critical property of a porous medium for the ways it affects fluid flow and static distributions. In oil reservoirs, capillary pressure delineates the water-oil and gas-oil transition zones and defines the variation of connate water saturation throughout the vertical rise. Capillary pressure controls the relative freedom of movement of the fluids during production, the shape of the interfaces, the influence of interfacial tension on recovery, fluid accumulation, vertical flow between communicating layers of different permeabilities, and the relative permeabilities of the fluids (Hassler et al., 1944; Brown, 1957). Capillary pressure also influences residual saturations and the mechanisms of fluid entrapment. The capillary control of microscopic fluid distribution also affects the macroscopic flow behavior. As was already mentioned, displacement efficiency in porous media is limited by the capillary forces in the way they determine the ultimate residual and irreducible fluid saturations. The capillary forces tend to oppose the segregation of continuous phases while gravity forces tend to segregate them (Buckley and Leverett, 1943). Capillary forces are the cause of the "boundary effect" where water blocks the oil flow rate a few feet around a wellbore producing at a low rate (Leverett, 1941).

In fractured reservoirs, capillary forces are the dominant force in the recovery of oil from matrix blocks. In the matrix, the rock permeability is substantially lower than the fracture permeability. Flow rates are reduced in matrix blocks and the capillary forces dominate over viscous and gravitational forces in the mobilization

of the oil. Capillary pressure is usually not the dominant mechanism of production but can affect the rate of production (Perkins, 1957; Leverett, 1941).

Although capillary pressure can affect or control recovery rates, it is not itself affected by the production rate in waterwet porous media (Perkins, 1957; Lebastie, et al., 1980). Capillary pressure is a function of pore size, pore shape, pore distribution, and the wetting characteristics of the rock (Hassler, et al., 1944). Capillarity is also affected by the fluid interfacial tension, saturation, and saturation history, as well as the textural properties of the rock surface (Brown, 1951). Measuring the capillary properties of a rock sample of reservoir rock, therefore, is important in maximizing petroleum recovery. The capillary pressure curve, the graphical relationship of capillary pressure and saturation, is a reflection of the distribution, orientation, shape, and tortuosity of the pores, the interfacial and interstitial surface area, and the relative permeability of the wetting phase (Rose and Bruce, 1949).

The development of the capillary pressure equation came out of Laplace's theory on the work required to move a fluid interface (Adam, 1968). If the interface is curved, movement of the interface outward, parallel to itself, requires work since the surface area of the interface expands. This work is supplied by the pressure difference across the interface. For a unit area, A , the additional area gained by movement of the interface is given by $A\delta n \left(\frac{1}{r_1} + \frac{1}{r_2} \right)$, where δn is the radius extension and r_1 and r_2 are the radii of curvature. The work done against the surface free energy is $\sigma A\delta n \left(\frac{1}{r_1} + \frac{1}{r_2} \right)$, where σ is the interfacial tension. The work done by the pressure difference is $\Delta P\delta nA$. Since the work done by the pressure

difference is equal to the work done against the surface free energy in expanding the interface surface area, Laplace's equation for capillary pressure becomes

$$\Delta P = \sigma \left(\frac{1}{r_1} + \frac{1}{r_2} \right)$$

For a capillary tube, the radii of curvature are equal. The effect of wettability can be added by introducing the contact angle, θ into the equation. The resulting equation for capillary pressure in a capillary tube is

$$P_c = \frac{2\sigma \cos \theta}{r}$$

Early theories on the capillarity of porous media treated the rock as a bundle of parallel capillary tubes. Leverett (1941) discarded this theory as insufficient to model pore structures.

There have been many attempts to correlate rock capillarity with permeability. The main reason for this is because, to some extent, as the pore size decreases both capillary pressure and permeability increase. Stahl and Nielsen (1950) reported a capillary pressure – permeability relationship, and Rosman and Simon (1976) explained flow heterogeneities like early water breakthrough and oil bypassing as effects of capillary pressure parameters, like pore size, shape, and distribution. Leverett (1941) established a functional relationship between capillary pressure and reservoir permeability and porosity. His functional group, later called the Leverett "J" function by Rose and Bruce (1949), can be used to correlate capillary pressure data on different core samples with the same lithology and from the same reservoir. The "J" function is a measure of the tortuosity of the flow channels and is given as (Leverett, 1941)

$$J(S_w) = \frac{P_c}{\sigma \cos \theta} \left(\frac{K}{\phi} \right)^{\frac{1}{2}}$$

The wettability term, $\cos \theta$, was added by Rose and Bruce (1949) but does not completely account for the wettability effects on capillary pressure. In fact, many investigators have studied and measured the effects of wettability on capillary pressure (Kinney and Nielsen, 1951; Jennings, 1957; Morrow and Mungan, 1971; Morrow, 1976). Morrow (1976) reported critical contact angles where capillary pressure becomes insensitive to wettability. For the drainage process, $\theta_{crit} < 50^\circ$, and for imbibition, $\theta_{crit} > 25^\circ$.

2.3.1.2 Centrifuge Method of Measurement

This section discusses the various methods to date which have been developed for measuring capillary pressure. Following this, the centrifuge method, in particular, will be described.

There have been many methods developed for the purposes of measuring capillary pressure and generating the capillary pressure – saturation curve. A recent publication compared these methods and made some sensitivity studies of the factors which influence them (Omoregie, 1986). A brief description of the various methods is given below. A more detailed description is provided of the centrifuge method which was employed in this research.

Leverett (1941) was the first to measure capillary pressure. Using a method he developed, called the gravity method (Collins, 1961), he measured capillary pressure as the height of water rise in an unconsolidated sand and measured saturation by resistivity. Hassler and Brunner (1945) developed the centrifuge method

for small consolidated samples, calculating the capillary pressure as a function of revolutions per minute and indirectly determining saturation by a graphical technique. At about the same time, the porous plate method was developed and improved by several investigators (McCullough et al., 1944; Thornton and Marshal, 1947; Bruce and Welge, 1947; Rose and Bruce, 1949). In the porous plate method, the use of a semi-permeable ceramic plate permitted the most precise and accurate determination of capillary pressure curves (Yuster and Stahl, 1984). Because of the tedium involved in the porous plate method (data collection may take more than one month to generate a single capillary pressure curve), a mercury injection technique was developed (Purcell, 1949). Mercury injection is the fastest and easiest method available but is not a direct measure of the capillary pressure between the reservoir fluids. A vapor pressure lowering technique was developed for measuring high capillary pressure measurements (Calhoun, et al., 1949) but is not frequently used. A dynamic method was developed in the wake of fears that static capillary pressure measurements would not apply to a dynamic system (Brown, 1951). Brown's method generated results in agreement with the mercury injection and porous plate methods, proving the applicability of static capillary pressure measurements to dynamic conditions. A constantly accelerating centrifuge technique was developed by Hoffman (1963) but is not favored over the original method of Hassler and Brunner.

If no capillary pressure data or means of measuring it are available, Mungan (Part 3, 1981) suggests a method for generating capillary pressure data from that of lithologically similar formations.

In general, the porous plate method is the most popular for accurate results. The aid of computers, however, has improved the saturation approximation in

the centrifuge method. Together with the reduction in time requirements, this advantage has placed the centrifuge method in a position to rival the porous plate technique.

After the development of the centrifuge technique by Hassler and Brunner, Slobod et al. (1951) further evaluated the method by comparing its results to that of the porous plate method (Slobod et al., 1951). They found a good correlation for the irreducible water saturation and concluded the advantages of the centrifuge method included:

1. reduced chances of not attaining equilibrium
2. better reproducibility
3. was theoretically sound
4. reduced time requirements
5. residual saturations are characteristic of reservoirs

Marx (1956) used the centrifuge to generate gravity drainage curves and found the centrifuge method to be a good approximation of natural gravity drainage in a laboratory column. A recent investigation by Mungan (Part 3, 1981) also found the centrifuge irreducible water saturation to be representative of actual reservoir values but suggested waterflooding (displacement) techniques to determine residual oil saturations.

The concern over residual oil saturations obtained by the centrifuge arose from the development of extremely high speed centrifuges capable of attaining unrealistic capillary pressures. Dombrowski and Brownell (1954) first suggested the existence of a gravitational limit above which continuous non-wetting phase distribution became segregated.

Others have investigated the basis for Hassler and Bruner's assumption of 100 % wetting phase saturation at the outlet end of the core (Wunderlich, 1985; Omoregie, 1986; O'Meara et al., 1988). There was concern that the gravitational forces would cause the non-wetting phase to displace some wetting phase from the outlet end of the core (Wunderlich, 1985) (Omoregie, 1986) (O'Meara et al., 1988). This would invalidate Hassler and Brunner's assumption that the outlet end of the core is saturated 100% with wetting phase. The bond number, the ratio of gravity forces over capillary forces, was measured at various rotational speeds in order to determine the point at which Hassler and Brunner's assumption might fail. A critical bond number of 0.50 was found to be an upper limit in the balance of gravity and capillary forces (O'Meara, 1988). Centrifuge drainages should be designed to maintain bond numbers less than 0.5. In addition, O'Meara found it necessary to use non-wetting endplates next to the core outface to maintain 100% wetting phase saturation at the outflow end of the core.

In an attempt to provide a quantitative estimate of centrifuge equilibration time, Hagoort (1980) found that late time production is a linear function of $t^{(\frac{1}{1-n})}$, where n is the Corey exponent.

An important part of the centrifuge method is the determination of the end-point saturation value. The following is the derivation of Hassler and Brunner's method. In the centrifuge, the average gravitational acceleration in the core can be expressed as the average centrifugal acceleration.

$$\bar{g} = \omega^2 \bar{r}$$

where,

\bar{g} = average gravitational acceleration

ω = rotational velocity (rad/sec)

\bar{r} = radius from rotational axis to middle of core

This approximation of an average acceleration across the core is valid if $\bar{r} \geq 2.33$ in. for a 1 in. core. According to Hassler and Brunner,

$$\bar{S} = \frac{1}{L} \int_0^h S(\rho g h) dh$$

where,

\bar{S} = average saturation

L = core length

S = endpoint saturation

ρ = density

g = gravitational acceleration

h = height of capillary rise in core

Since capillary pressure is defined as the difference between non-wetting phase pressure and wetting phase pressure, $P_c = P_{nw} - P_w = (\rho_{nw} - \rho_w)gh = \Delta\rho gh$. If the following variables are defined:

$$z = \Delta\rho g L = \Delta\rho \omega^2 \bar{r} L = P_c @ L$$

$$x = \Delta\rho g h = \Delta\rho \omega^2 \bar{r} h = P_c @ h$$

$$dx = \Delta\rho g dh$$

$$dh = dx / (\Delta\rho g)$$

then,

$$\begin{aligned}
\bar{S} &= \frac{1}{L} \int_0^z \frac{S_x}{\Delta \rho g} dx \\
&= \frac{1}{\Delta \rho g L} \int_0^z S_x dx \\
&= \frac{1}{z} \int_0^z S_x dx \\
z\bar{S} &= \int_0^z S_x dx
\end{aligned}$$

taking the derivative with respect to the upper limit of the integral,

$$\frac{d(z\bar{S})}{dz} = S_z$$

Plotting $z\bar{S}$ vs. z , $S_z = \text{slope at } z = \frac{d(z\bar{S})}{dz}$. Using the slope of the first plot as S_w , it is then possible to generate an endpoint capillary pressure curve, P_{cL} vs. S_w .

To improve upon this approximation of S_w , there have been many numerical techniques introduced to differentiate the $z\bar{S}_w$ vs z curve. This may offer some improvement over graphical techniques but usually generates curves with too much scatter and must be manually smoothed. Melrose (1988) recently compared the Hassler and Brunner solution to Van Domselaar's solution and found the Hassler and Brunner solution was preferred at low saturations and the Van Domselaar solution at high saturations and with long cores. The numerical method developed by Bentsen and Anli (1977) parameterizes the saturation as a function of capillary pressure. In their model, they express capillary pressure as a function of normalized saturation, displacement pressure, and a constant of proportionality

which incorporates wettability, interfacial tension, and pore size distribution. The advantage of their method, among other things, is that the solution is determined by integration instead of differentiation and requires less time and effort. The disadvantage is the necessity for an accurate mathematical model. The Bentsen and Anli model has been known to fail when the capillary pressure curves have a downward turn near $S_w = 1$ and it may underestimate P_{cD} (Skuse et al., 1988).

2.3.2 Fluid Recovery Mechanisms

The recovery of oil from porous media occurs as a displacement process. Water or gas or both invade a pore containing oil and force it to move out and into another pore. The displacement of oil in a pore is usually unidirectional, meaning the oil moves out a different pore throat than the one in which water or gas is entering. Gas may sometimes be counter-currently displaced, leaving a pore through the same pore throat the displacing fluid enters. Eventually, the oil or gas flows through large pore channels. Multiphase fluid movement is governed by many parameters. Principly, they include permeability, wettability, capillary forces, gravity forces, viscous forces, and pressure forces.

As was described briefly in the discussion of the USBM method for wettability measurement, there are two processes of displacement: imbibition and drainage. Imbibition is the process by which wetting phase displaces non-wetting phase, like water displacing oil. Drainage is the process by which non-wetting phase displaces wetting phase, like gas draining oil, or oil displacing water. In strongly water wet

rocks imbibition is a spontaneous process and drainage requires an applied force, like pressure, to move the interface through the pore. .

Since water always exists in a water wet reservoir rock, the imbibition process can be thought of as a front – like increase in water saturation moving across the rock (Handy, 1960). Water fills the small interstitial spaces, like small pores, the corners of large pores, or the pendular ring around around the grain contact. As water saturation increases, the pendular rings interconnect to form a mesh of tortuous pathways for water flow. In small pores the water displaces non-wetting phase completely, leaving only water. In larger pores, the water may displace the oil slowly by thickening the water film over the sand grains and thinning the oil stream at the center of the pore. Eventually, the oil is completely displaced from the pore. In glass bead pack experiments, after an imbibition, pores will contain either oil or water (Gorring, 1978). Only in mixed wettability rocks has it been observed that a surface film of oil can be left behind and not be displaced completely from a pore (Salathiel, 1973). The reason imbibition occurs spontaneously is because water has a lower surface free energy than oil or gas. As water displaces oil, the surface free energy decreases and spontaneously propagates the water through the porous media. The rate and amount of imbibition is affected by wettability, interfacial tension, pore structure, permeability, initial saturation, fluid viscosity, and saturation history (Dullien, 1979; Richardson, 1961). Imbibition rates are commonly measured in small core samples. Early experimentation has shown that small core imbibition results in residual oil saturations similar to that in long core floods (Moore and Slobod, 1956).

The drainage process works against spontaneous imbibition. Since water exists in the small spaces and pore throats, oil or gas displaces water by moving the

interface from the pore body, through the pore throat, and across the next pore body. The maximum curvature of the interface passing through the pore throat represents the upper limit of configurational stability (Melrose, 1965). Once past that point, the interface is unstable and the surface free energy is favorable to propagate the interface through the next pore body and up to the next pore throat(s). This "jump" was observed as water evaporated from a pile of tapered capillary tubes. Water drained around the tubes slowly but through the tubes in instantaneous jumps called Haine's jumps (Morrow, 1970). Wettability has been shown to have little or no effect on S_{wir} by some investigators (Harris et al., 1963-64; Morrow 1971; von Engelhardt, 1955) whereas others reported S_{wir} is dependent upon wettability (Bethel and Calhoun, 1953; Iwankow, 1960). Usually in water wet consolidated sandstones, water wetness increases S_{wir} over fractionally or intermediate wet rocks.

2.3.3 Residual Fluid Trapping Mechanisms and Distribution

In water wet rocks, water is never discontinuous. There always exists an interconnected film or channel of water through the pores. Therefore, water can never be "trapped" by oil or gas. Oil or gas will flow when continuous saturation patterns exist, but may become trapped if the thinning channel of fluid snaps off and retreats into the pore body to form a gas bubble or oil globule (Wyckoff and Botset, 1936). The residual oil globules are discontinuous blobs usually a few pores in length and exist throughout the entire range of pore sizes (Pickell et al., 1966). Oil can also be trapped by water preferentially entering smaller pore channels around the oil and, essentially, bypassing the oil, cutting it off, and

completely surrounding it (Chatzis et al., 1983). Gas bubbles are trapped only behind an encroaching water front (Handy, 1960). As water saturation increases, the relative permeability of the gas decreases and the gas is left behind the front, eventually pinched off to form a bubble in the pore body (Geffen et al., 1952). The ultimate residual saturation of a non-wetting phase is a function of the capillary number, the ratio of viscous to capillary forces. Residual saturations have also been reported to be dependent upon imbibition rate, saturation history, and the distribution of non-wetting phases (Handy, 1960; Raimondi, 1964). As long as diffusion may occur, these globules or bubbles which exist as a residual saturation are not stable but can be considered so if diffusion is negligible (Hassler et al., 1944).

The size and distribution of residual oil saturations is usually dependent upon the rock wettability (Donaldson and Thomas, 1971). Many other factors will effect it, including the production rate, but capillary forces are often dominant. The best measure of those factors which affect residual saturations is the capillary number. The capillary number is the ratio of capillary forces to viscous forces and is indicative of the rate effects, interfacial tension effects, and the wettability effects. Although oil wettability usually implies higher residual oil saturations, it is possible for lower residual oil saturations to be found in weakly water wet rocks, depending on the continuity of the oil wet surfaces (Rathmell et al., 1973). The distribution of non-wetting phase tends to be dendritic (Goddard et al., 1962) in water wet sandstones and more film-like in the sandstones with mixed wettability (Salathiel, 1973).

2.4 Effect of Third Phase on Fluid Behavior

2.4.1 Capillary Pressure

The earliest recorded investigation of three phase capillary pressures was performed by Leverett (1941). He concluded that a three phase system may be treated as a series or combination of several two phase systems which still follow the same laws of normal two phase capillarity in porous media. Furthermore, he found the gas – oil interface behaved as if the third phase was not present. This was explained because a gas – liquid interface is bound by the pore geometry of the porous media. Other investigators have also reported that three phase systems can be assumed as several two phase systems. Efros (1958) observed that the presence of gas did not affect oil – water capillary pressure in water wet rocks. Work performed by Dougherty and Sheldon (1964), Kyte et al. (1956), and that of Efros all showed that as long as a water – oil interface does not “catch up” to a gas – oil interface, then two phase capillary pressure data can be used for each bank. Kyte et al. (1956) found that even when mobile saturations of gas were present with the oil and water, gas would become immobile and the system could again be assumed as only containing two phases (Kyte et al., 1956). These findings are supported by Hassler et al’s (1944) observation that three phase capillary pressures are dependent upon the same parameters as two phase capillary pressures.

Although some work has been performed in the area of the effect of gas saturation on oil recovery by waterflood, there has been little further investigation of three phase capillary pressures. It has been common to use two phase capillary pressure data when three phase data was needed or could be applied. Since the recent publication of some important findings by Kantzas and Chatzis in the study

of gravity drainage, interest in this area has begun to grow (Kantzas et al, 1988; Chatzis et al., 1988).

2.4.2 Fluid Recovery Mechanisms

Although research in the recovery mechanisms of three phase reservoirs is extremely limited, there is little disagreement about which mechanisms are involved. In the presence of gas and water, mechanisms of oil recovery can differ from those of recovering oil blobs isolated in a single continuous phase. Recently, Kantzas et al. (1988) pointed out that when air displaces oil and water, as in a gravity drainage, there are four possible mechanisms of displacement. Namely,

1. air displaces water which displaces oil
2. air displaces oil which displaces water
3. air displaces water; no oil moved
4. air displaces oil; no water moved

The first mechanism is never observed. In a controlled drainage, mechanism # 2 is observed. This was recorded in the free drainage of an unconsolidated sandpack saturated with water and discontinuous oil. Initially, the water bypasses the oil and air displaces the water only as in mechanism # 3. Then air displaces oil and the oil displaces water. Shortly after, the oil begins to form an oil bank; and as in mechanism # 4 air displaces the oil without moving the water in the oil bank. In short, gas approaching an oil blob surrounded by water saturated pore throats will leak the water until it reaches the oil. Then gas will displace the oil. Imbibition will not occur.

The mechanism of this displacement is believed to be film flow (Dumore, Scholls, 1974; Chatzis et al., 1988). In the presence of water and gas, oil tends to be displaced by the encroaching gas as a thin film of oil between the water and gas phases. Gas invades the water bypassed pores and displaces the oil to the film in larger pore channels. Recovery of this oil occurs as continued drainage decreases the film thickness.

Where a trapped gas phase was present as gas displaces oil in the presence of water, an oil bank forms behind an air bank (Chatzis et al., 1988). In this case where all three phases are present before drainage begins, gas displaces the oil which displaces the trapped gas in the form of a gas bank, which in turn displaces the mobile water.

It should be noted that these mechanisms of oil recovery by gas can only be achieved at low flow rates. At high flow rates gas fingering occurs due to its relative mobility and isolated oil blobs remain trapped unless the process is carried out long enough for diffusion to occur. Practically, however, this is not possible.

Not surprisingly, no research has been published on the recovery of mechanisms of gas or water in three phase reservoirs since the recovery of oil is the primary focus of modern petroleum research.

2.4.3 Residual Fluid Trapping Mechanisms and Distribution

There has been little experimental investigation into the effect of the presence of a third phase on the mechanisms of fluid entrapment and the resulting distribu-

tions of residual fluids. To date, research in this area has focused on two processes: water flooding oil reservoirs with free gas present, and gravity drainage.

Gravity drainage is the drainage of oil by gas. It is often used as an efficient mechanism of recovery in thick formations with good vertical permeabilities. Gravity drainage can provide residual oil saturations as low as 8-10%, much lower than common water flood residual oil saturations of 30-60% (Leverett, 1941). A recent experiment by Carlson (1988) showed that the presence of water had no effect on the residual oil saturation value. Earlier, it was also found that the presence of water did not affect the recovery of a miscible gas displacement unless the water was simultaneously injected (Tiffin, Yellig, 1983). Hagoort (1980) concluded that the gravity drainage process can be described by a two phase flow approach if the connate water saturation is low. As the water saturation increased, he found oil permeability increased and thus oil recovery increased, as the flow channels became more streamlined. In general, the industry has taken the opinion that the presence of water does not affect the gravity drainage process, and, therefore, does not affect residual oil saturations or trapping mechanisms.

There has been much qualitative investigation into the benefit of free gas present during a water flood. Many investigators have concluded that the residual oil saturation is reduced by the presence of free gas trapped in the oil zone (Holmgren, Morse, 1951; Kennedy, Guerrero, 1954; Kyte et al., 1956; Neilson, Flock, 1962; Marsden, 1965; Frauenfeld et al., 1988). For low gas saturations, the effect was found to increase with increasing free gas. At high gas saturations, increasing gas saturation was found to increase the residual oil saturation (Kennedy, Guerrero, 1954) or to have no effect at all (Kyte et al., 1956). In any case, an optimum

gas saturation was believed to exist. The optimum saturation was estimated to be equal to or less than the critical gas saturation (Marsden, 1965), or exactly 8% (Neilson, Flock, 1962). The recovery increase was attributed to the expansion effect of the gas occupying pores which otherwise might trap oil (Holmgren, Morse, 1951). The volume reduction of oil was found to be equal to or less than the volume increase in gas (Kyte et al., 1956). Other factors contributing to the reduction in residual oil saturation were the additional gas drive, production of oil mist with the gas phase, and changes in the physical characteristics of the oil (Holmgren, Morse, 1951). Counteracting these factors are the shrinkage of the oil caused by the release of solution gas, increases in oil viscosity as oil pressure decreases, and a reduction in oil permeability (Kyte et al., 1956). No effect was found of the gas saturation on the capillary pressure between oil and water.

3. Experimental Program

3.1 Method of Study

The project undertaken was to measure two and three phase capillary pressure curves in a consolidated sandstone using the centrifuge. The saturation histories studied for both two phase and three phase measurements are given as follows:

Gas – water capillary pressure

1. primary drainage of water by oil
2. primary drainage of oil by gas
3. primary imbibition of water
4. secondary drainage of water by gas
5. secondary imbibition of water
6. tertiary drainage of water by gas

Oil – water capillary pressure

1. primary drainage of water by oil
2. primary drainage of oil by gas
3. primary imbibition of water
4. secondary drainage of water by oil
5. secondary imbibition of water
6. tertiary drainage of water by oil

Gas – oil capillary pressure

1. primary drainage of water by oil

2. primary drainage of oil by gas
3. primary imbibition of oil
4. secondary drainage of oil by gas
5. secondary imbibition of oil
6. tertiary drainage of oil by gas

In all cases, the core was initially saturated 100% with water and then drained by oil to S_{wi} . This process mimics that which occurs in the reservoir to establish a connate water saturation. After the oil drainage of water, the oil is drained by gas. For gas – water measurements, this establishes a residual oil saturation. For oil – water measurements, the gas is reduced to a residual or trapped saturation by water imbibition. For gas – oil measurements, the irreducible water saturation was established by the primary oil drainage. Secondary and tertiary drainages were then carried out.

3.2 Materials Used

The core selected for the experiments was a 250 md, slightly heterogeneous, consolidated Berea sandstone. The porosity of the sandstone was 17.2%. All cores were cut from the same block of stone to the dimensions of 1 in. long and 1 in. in diameter for use in the centrifuge. The cores were then fired in a furnace at 300°C for 12 hours to deactivate any clays in the core. The cores were saturated and then used in the centrifuge experiments. Because the same core must be used for both the two phase and three phase experiments, a core cleaning procedure was

developed to clean out the brine and oil. Cores were cleaned in a soxlet extractor first by toluene, then by acetone, and then dried in a oven at 180°C.

The water phase was a deaerated 2% NaCl brine solution. The use of brine was necessary to help prevent any hydration of the clays in the rock.

The oil phase was standard grade kerosene which was passed through a 24 in. silica gel column at a rate of 3 cc/min to remove any polar compounds. The existence of polar compounds in the oil could cause wettability changes during the experiment. The kerosene was also deaerated.

The interfacial tension between water and air measured 71 dynes/cm, between oil and air was 62 dynes/cm, and between oil and water was 15 dynes/cm. These values were obtained from measurements made with a platinum ring tensiometer.

3.3 Equipment and Procedures Used

The centrifuge used in the experiments was a Beckman model L8-M60/P. The bucket assembly of the centrifuge rotor which holds the core is shown in Figure 1. The centrifuge was not equipped for automated reading of the interface. After stabilization at a given rotational speed, a strobe illuminator positioned under the rotating bucket enabled the manual reading of the interface in the graduated receiving tube.

The imbibition process was carried out in an apparatus as is shown in Figure 2. The funnel was constructed of glass with a scribe mark indicated on the stem.

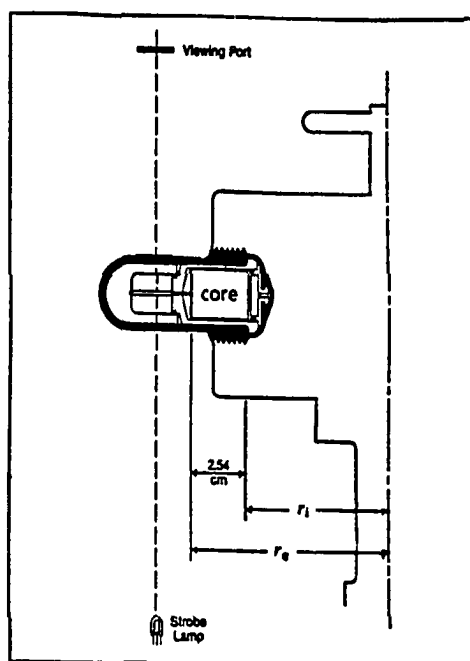


Figure 1. Centrifuge Bucket Assembly (after Skuse, Beckman Inst.)

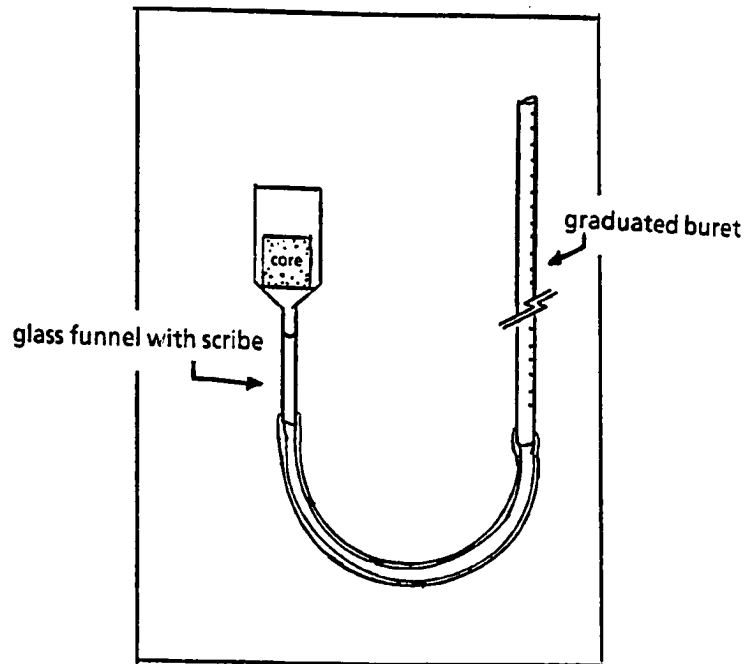


Figure 2. Free Imbibition Assembly

A modified version of this funnel was used for the water displacing oil imbibitions. This funnel had a volumetric scale scribed on the stem to enable direct measurement of the oil produced. This was done to enable a calculation of any trapped gas produced as well. The funnel was first wet with the imbibing fluid then "zeroed" by bringing the interface in the funnel down to the scribe mark on the stem. The initial level of the interface in the buret was recorded. The core was then placed in the funnel and the buret raised to permit complete coverage of the core in wetting phase. The core funnel was then covered to prevent evaporative losses. Readings could be taken periodically to determine the end of the free imbibition. Water imbibition took less than 24 hours and oil imbibition took about 48 hours. By bringing the fluid level back down to the initial scribe mark, a second buret reading could be taken by recording the volume of the oil produced in the funnel. The gas produced (not trapped gas) was equal to the difference between the two buret readings. If any of the gas trapped in the water or oil was produced during imbibition (gas was trapped in the core for the three phase oil - water measurements), the amount of gas produced could be determined by weight.

The cores were saturated in a vacuum system by placing them a few at a time in a canning jar fitted with a large rubber stopper with two holes drilled. A separatory funnel was placed above the cores, through one of the holes. The vacuum source was connected through the other hole. After sustaining a 500 micron vacuum for about 8 hours, the separatory funnel was filled with brine and allowed to drain over the cores until they were covered. The vacuum was then released and the cores were allowed to imbibe for at least 12 hours. Forced imbibition under brine in the centrifuge did not produce any air from the cores and they were determined to be completely saturated.

4. Experimental Results and Discussion

Capillary pressure measurements were performed as described in Chapter 3. The results from each run were collected by physical observation and are summarized in the Appendix. Using the method of Hassler and Brunner (1945), endpoint saturations were determined graphically and capillary pressure curves were constructed for secondary and tertiary drainages. The figures 3 - 13 presented in this chapter were constructed using an RSPLINE curve fit. To determine the effect of the presence of a third immobile phase on capillary pressure between two mobile phases, both two and three phase measurements were made of Gas - Water capillary pressure and Oil - Water Capillary pressure. However, as explained in Chapter 3, only three phase measurements were made of gas - oil capillary pressure. A complete analysis of the curves included

1. an analysis of each separate curve
2. the determination of capillary pressure hysteresis
3. the determination of the effect of the presence of a third phase on capillary pressure

The determination of the effect of the presence of a third phase on capillary pressure includes the effect of the presence of a third phase on

1. the shape of the capillary pressure curve
2. the irreducible water saturation
3. the residual oil or gas saturation

Also discussed is the effectiveness of the core cleaning process used to clean the cores in between experiments.

4.1 Gas – Water Capillary Pressure

The secondary and tertiary drainage curves for a core containing only gas and water are presented together in Figure 3. The shape of the curves are very characteristic of a Berea sandstone. The saturation at zero capillary pressure is the residual gas saturation ($1 - S_{gr}$) after imbibition. The portion of the curve just above zero capillary pressure is indicative of the number of large pores in the rock. The diffused or flat midsection of the curve is a measure of the heterogeneity of pore sizes. The upper region of the curve approaches $S_{w_{ir}}$ asymptotically. This particular sample Berea sandstone is a slightly heterogeneous rock. This is exemplified by the diffused shape of the capillary pressure curve. Very homogeneous cores may exhibit a nearly horizontal mid section in the curve. The rise in capillary pressure of about 1 psia with little change in saturation at the bottom of the curve shows there are relatively few large pores. The biggest change in saturation per increase in drainage capillary pressure is above 1 psia. This implies a much greater number of pores are associated with capillary pressures in the range of 1 - 3 psia than below 1 psia. The basic shape of the curves in figure 3 is virtually the same shape found for all the curves presented. Some other tertiary drainage curves, however, lose their inflection point and become more homogeneous. This is addressed in another section of the discussion.

Overall, the curves show a good reproducibility of the drainage process. There is a separation in the saturation values of approximately 5% above 2.5 psia capillary pressure which resulted in a similar difference in the irreducible water saturation ($S_{w_{ir}}$) values. A difference of 5% in saturation can be attributed predominantly to errors incurred in the graphical determination of endpoint water

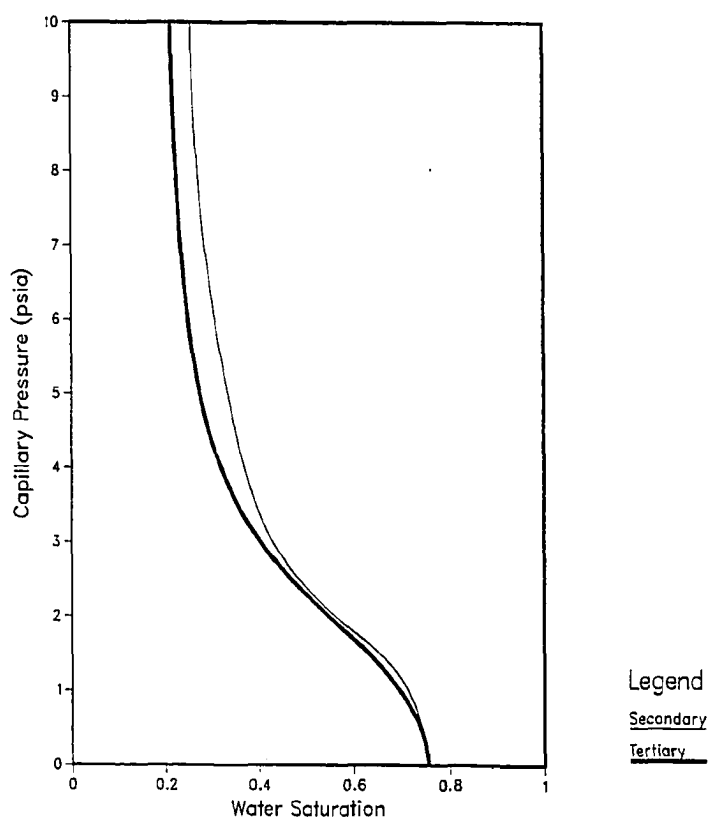


Figure 3. Gas - Water Capillary Pressure
Two Phase Secondary and Tertiary Drainage

saturation. As is discussed in section 4.6, small irregularities in the smoothness of the $z\bar{S}_w$ vs. z curve or even slightly erratic data can cause an error in the saturation value of several percent, especially at mid to high range values of capillary pressure.

The three phase drainage curves are shown in Figure 4. As was true for gas draining water, the process of gas draining water in the presence of (8%) residual oil is a fairly reproducible process. The small difference in saturation values between the two curves is only about 3%, which lies within the limits of experimental error. The S_{wir} was approximately the same for secondary or tertiary drainage and the S_{gr} was exactly the same. One characteristic of the tertiary drainage curve worthy of note is that its shape is slightly more diffused than the secondary drainage curve. This hysteresis in the tertiary curve may imply the existence of some trapped air in the core after the secondary imbibition. If so, air bubbles trapped in water in the larger pores could reduce the force required to displace the water – air interface through the large pore. This would diffuse the lower portion of the curve to lower water saturations. At higher rotational speeds, the bubbles are no longer trapped and, therefore, have no influence on the shape of the curve. A second possible explanation is that the trapped oil was slightly redistributed to a more uniform distribution during the secondary drainage and/or free imbibition. This would imply that gas drained some oil out of the larger pores and into some intermediate pores during the secondary drainage, and/or water forced oil out of some smaller pores into some more intermediate pores during the secondary imbibition.

To compare the three phase curves to the two phase curves it was helpful to superimpose one curve upon another, as was done in the previous figures. Figure

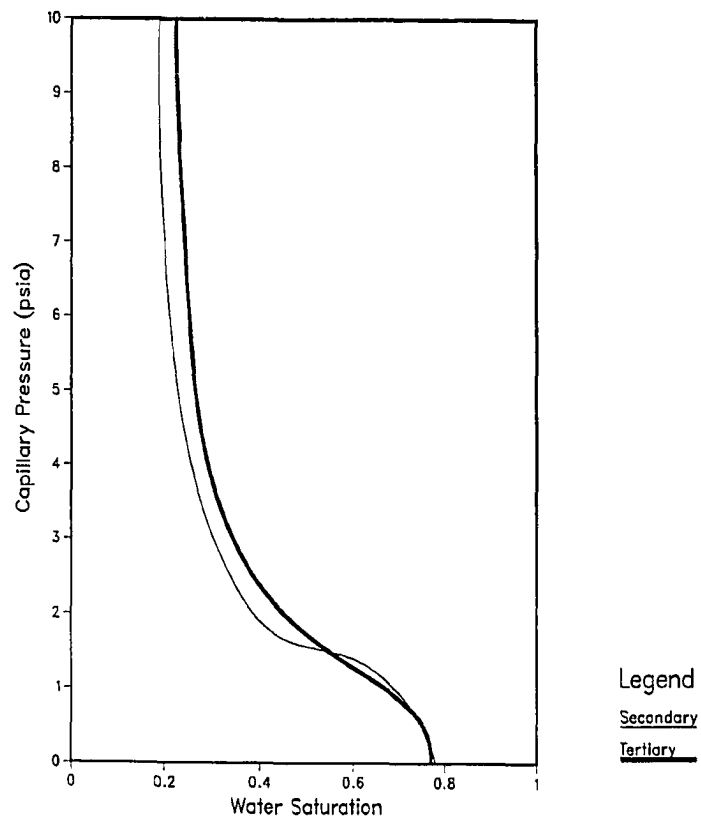


Figure 4. Gas - Water Capillary Pressure
Three Phase Secondary and Tertiary Drainage

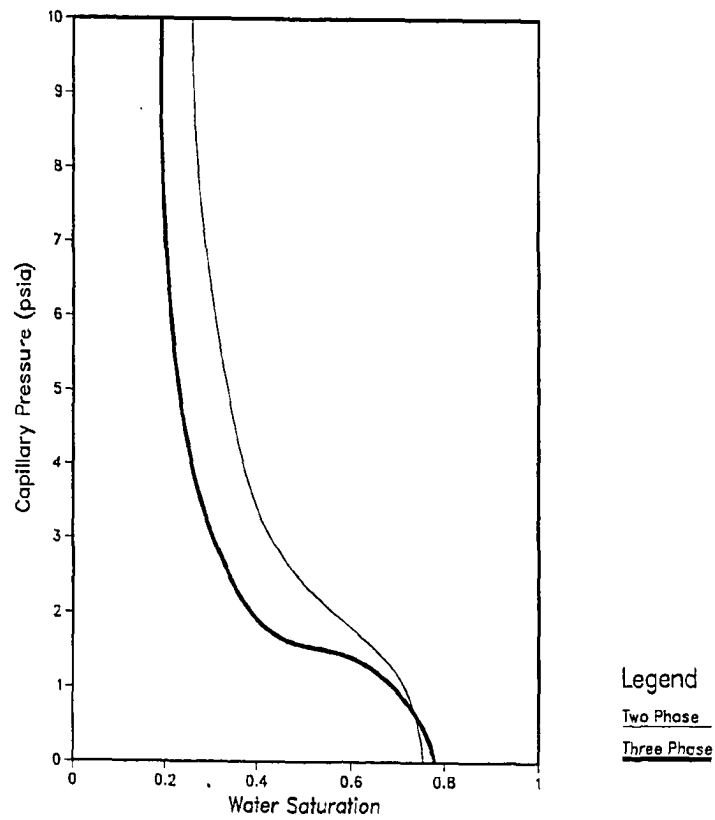


Figure 5. Gas - Water Capillary Pressure
Two Phase and Three Phase Secondary Drainage

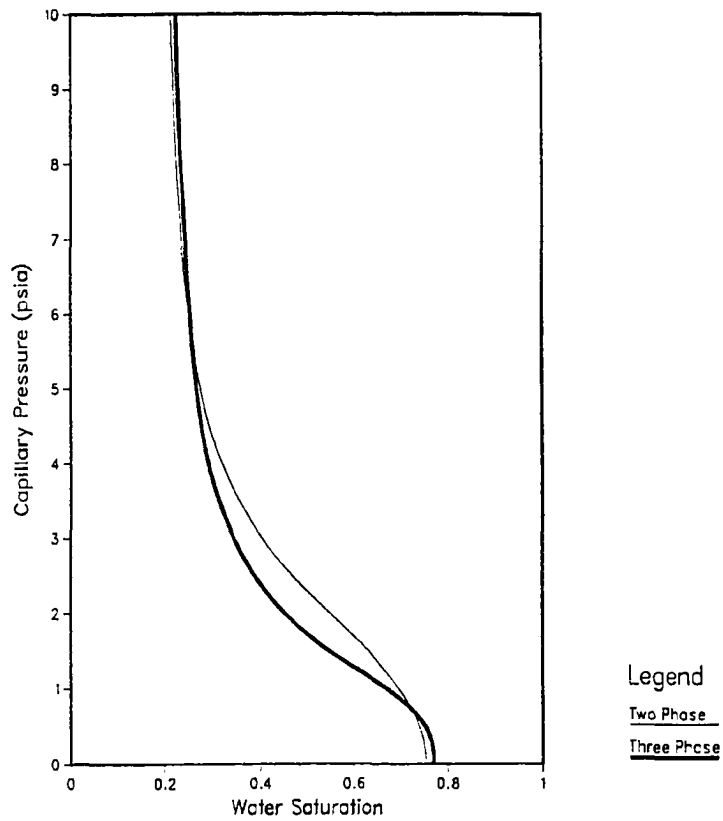


Figure 6. Gas - Water Capillary Pressure
Two Phase and Three Phase Tertiary Drainage

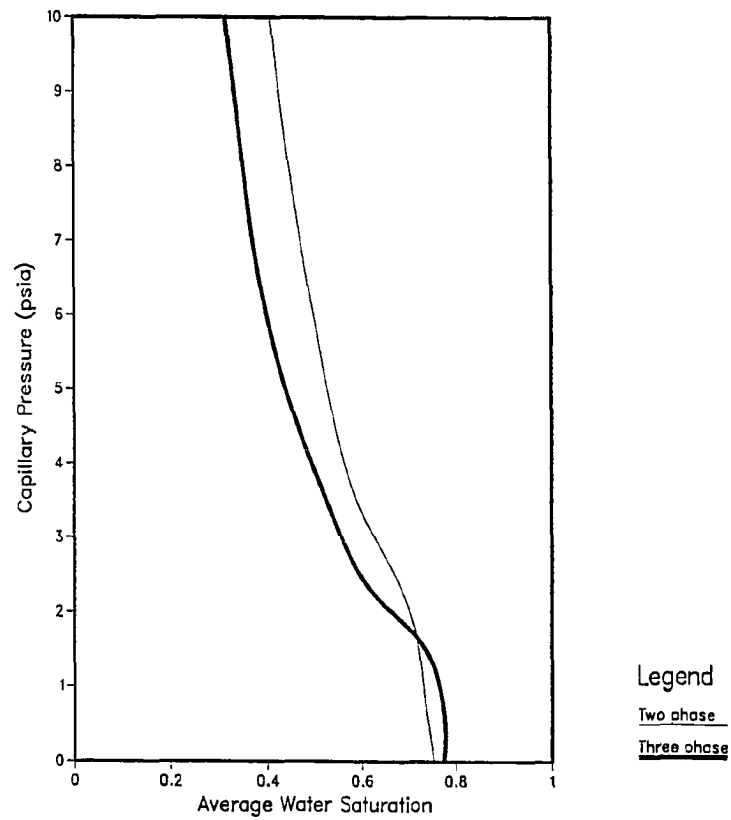


Figure 7. Gas - Water Capillary Pressure vs. Average Saturation
Two Phase and Three Phase Secondary Drainage

5 shows the secondary drainage curves for both the two and three phase cases. Figure 6 shows the tertiary drainage curves. In analyzing the curves, it is clear that the presence of oil did not affect the value of S_w after the imbibition of water into a gas saturated core. This can be explained by its history. The core, initially saturated 100% with water, was first drained by oil to $S_{wi,r}$ and then the oil drained by gas to S_{or} . During the primary imbibition, water displaced gas to S_{gr} in the presence of S_{or} . The residual non-wetting phase saturation after imbibition (in this case, $S_{or} + S_{gr}$) is the same as the residual non-wetting phase saturation after imbibition for the core containing only gas and water. In other words, a gas saturated core imbibing water will continue to imbibe until the water saturation reaches a particular and consistent fraction of the total pore volume. The presence of S_{or} in the three phase core does not affect this value of S_w but merely takes the place of some of the residual gas. The sum of S_{or} (8%) and S_{gr} (15%) in the three phase core is very close to the two phase S_{gr} of 25%.

In analyzing the shape of the curves in Figure 5, the presence of oil clearly reduced the heterogeneity of the pore spaces. Oil filled up the smallest pores which were not filled by water, leaving a relatively small range of pore sizes available for gas invasion. During the secondary drainage of water by gas (in the presence of trapped oil and gas) the oil was redistributed. This causes a shift in the position of the diffused portion of the three phase curve to a slightly lower capillary pressure. This supports the idea that the residual oil is remobilized by the gas during the drainage process and/or by the water in the imbibition process. The tertiary drainage curves in Figure 6 also show a decrease in pore size heterogeneity but the $S_{wi,r}$ values were the same (23%) for both the two phase and three phase cores.

From non-reproducible S_{wir} values in the secondary drainage and the small change in the distribution of pores available for gas invasion in both the secondary and tertiary drainages, it can be concluded that the presence of oil has had an effect on capillary pressure. This implies that the drainage process in the three phase core is not the same as the drainage process in the two phase core. If the oil had no effect, the two curves in Figures 5 and 6 should be the same shape. To further explain this effect, the capillary pressure was plotted against the average water saturation as opposed to the endpoint saturation. If the oil does not affect the drainage of water by gas, then one would expect the P_c vs. S_{wavg} curves (two phase and three phase) to have the same shape. In the region above approximately 3 psi and below 1 psi capillary pressure, this is true. However, just above the entry pressure of the core, it is clear that the oil has affected the capillary pressure relationship between gas and water in the presence of (8%) residual oil. An analysis of the average water saturations in the core after secondary imbibition showed that more water was drained from the drainage with oil present than the drainage without oil present. Oil, therefore, is moving within the core and draining water. This means that the technique of Hassler and Brunner for determining the endpoint saturation is invalid for cores containing three phases of fluids.

4.2 Oil – Water Capillary Pressure

The secondary and tertiary capillary pressure curves for the two phase oil-water system are shown in Figure 8. Like the gas-water curves, superimposed, there is little difference between the two curves. Except for a slight separation below 1 psia, the curves are identical. This separation is indicative of a decrease in the heterogeneity of pore sizes available for oil invasion. The irreducible water saturation, $S_{w,ir}$, was approximately 10% and the residual oil saturation, S_{or} , measured 45% in both drainages. It is important to note that the wettability of the samples was not affected by the core cleaning process nor the oil residence time. Typical of capillary pressure curves for oil and water, the flat portion of the curve occurs at a lower capillary pressure than in the gas-water curves.

Three phase capillary pressure curves are plotted in Figure 9. Upon examining the shape and hysteresis of the secondary and tertiary drainage curves for the three phase cores, it was determined that the presence of the gas had a very limited effect. The difference in the final value of S_w after primary and secondary imbibition is caused by the fact that, in the primary imbibition, water was displacing gas; in the secondary imbibition, water was displacing oil. The result is a higher residual saturation of non-wetting phase after secondary imbibition than after primary imbibition. In the analysis of the three phase curves, it was again helpful to juxtapose the two phase curves with the three phase curves. The two secondary drainage curves (two phase and three phase) are plotted in Figure 10 and the two tertiary drainage curves are in Figure 11. Figure 12 is a plot of capillary Pressure vs. Average water saturation.

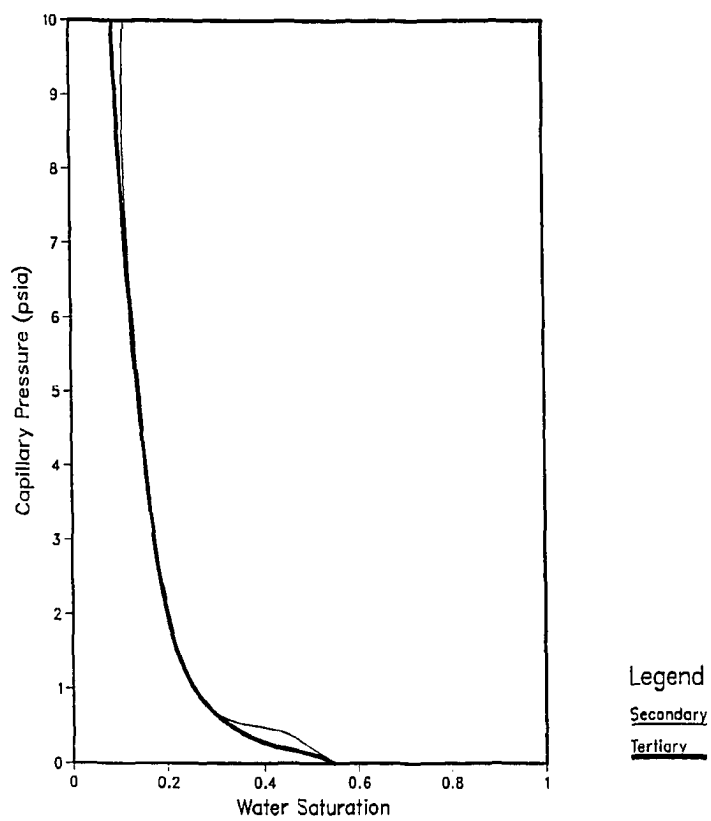


Figure 8. Oil - Water Capillary Pressure
Two Phase Secondary and Tertiary Drainage

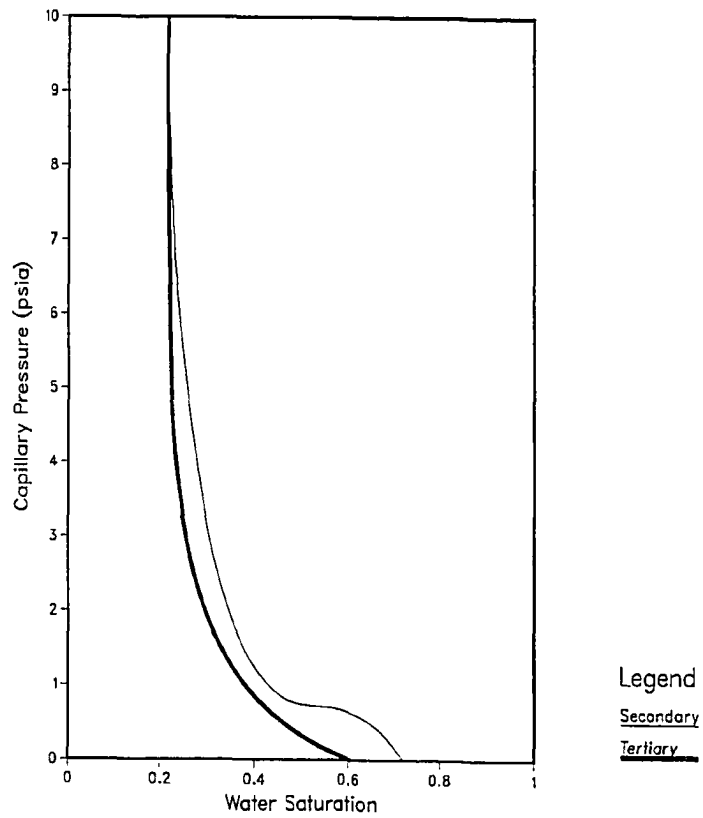


Figure 9. Oil – Water Capillary Pressure
Three Phase Secondary and Tertiary Drainage

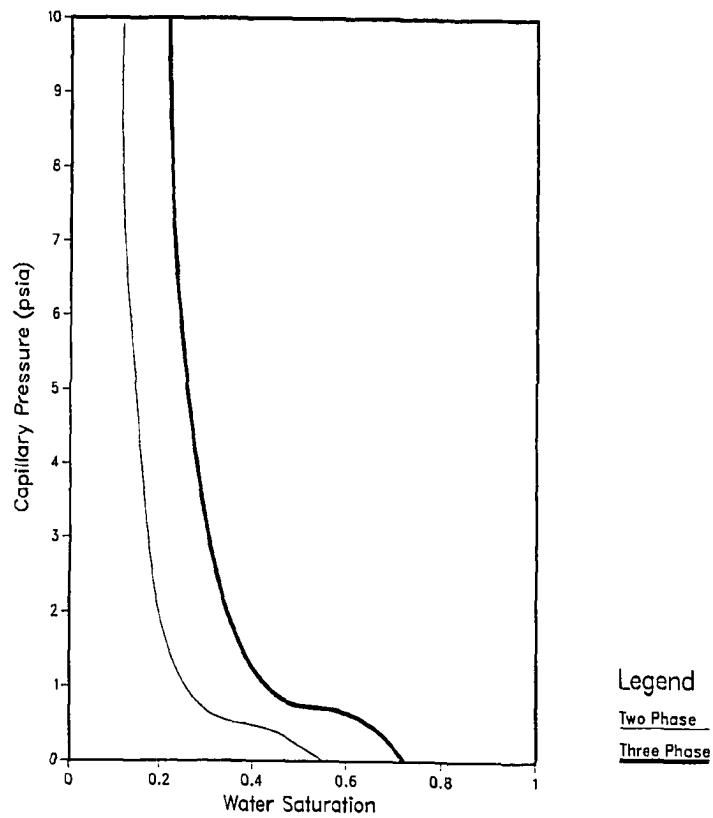


Figure 10. Oil - Water Capillary Pressure
Two Phase and Three Phase Secondary Drainage

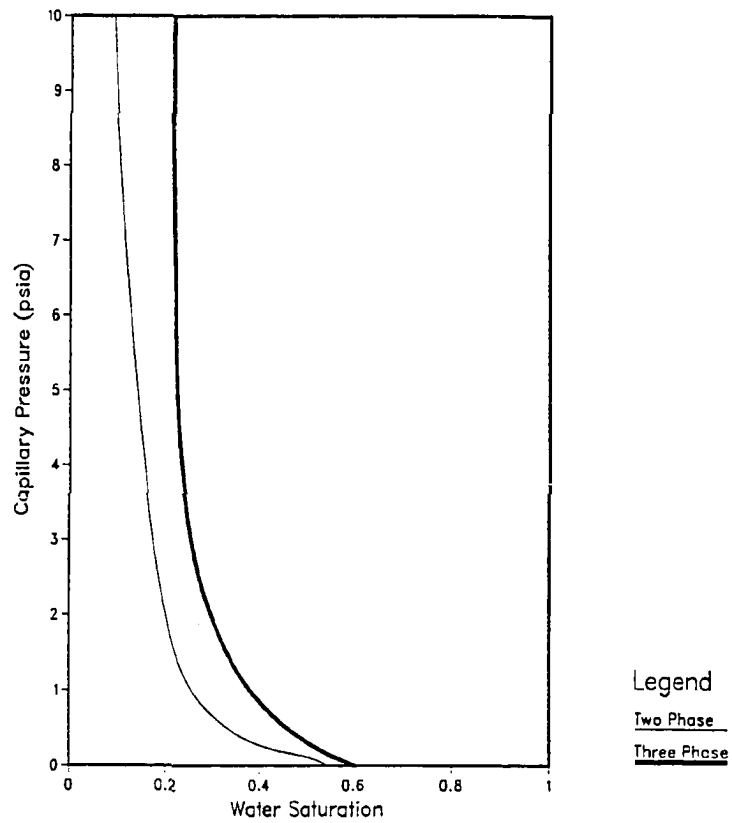


Figure 11. Oil - Water Capillary Pressure
Two Phase and Three Phase Tertiary Drainage

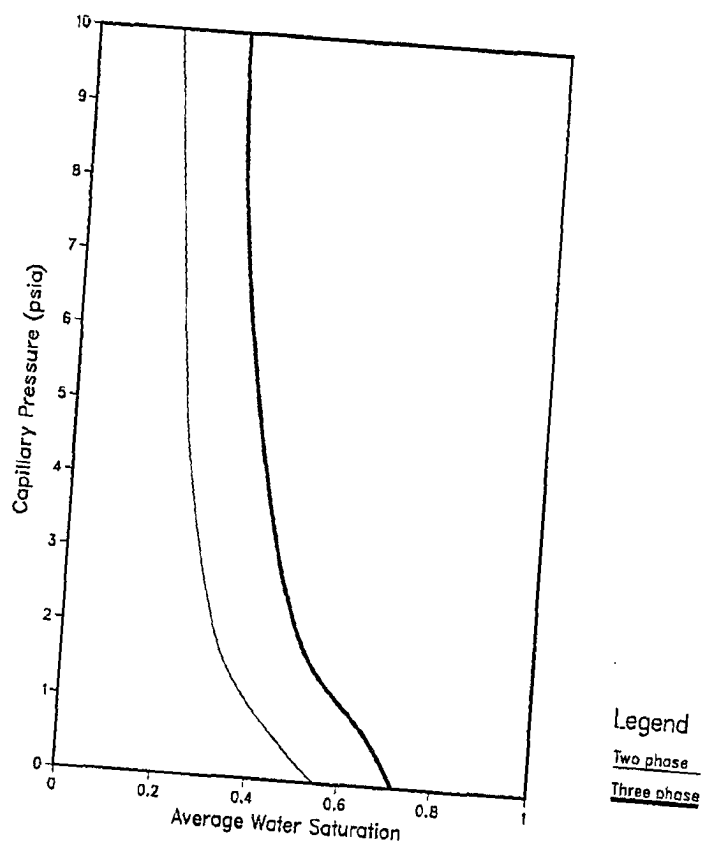


Figure 12. Oil - Water Capillary Pressure vs. Average Saturation
Two Phase and Three Phase Secondary Drainage

Comparing the two secondary drainage curves, the three phase curve is offset from the two phase curve by about a 15% margin of water saturation without any change in the shape of the curve. Similarly, the three phase tertiary drainage curve is offset from the two phase curve by a margin of approximately 10% with little change to the curve shape. In the secondary drainage curve, the presence of about a 20% gas saturation has a marked affect on the S_{wir} by doubling the two phase S_{wir} of 10%. It is difficult to explain such a large increase in S_{wir} , but it is believed that this is caused by the way in which the gas was trapped. Because the trapped gas saturation was established by water imbibition, the gas bubbles were trapped in the water, not the oil. It is theorized that the gas bubbles exist in the isolated large pores surrounded by water saturated small pores and pore throats. During oil drainage, oil entered the larger water saturated pores and displaced the water they contained but bypassed the pores locking in gas bubbles. In a sense, the trapped gas took the place of some of the oil in the same way that the residual oil took the place of some of the gas in the preceeding imbibition. However, gas is not as efficient a displacing fluid as oil is because of its higher interfacial tension with water. This means that some water which oil would have displaced relatively efficiently in a two phase system is now less efficiently displaced by gas. The pores trapping gas bubbles would therefore contain more water (thicker grain covering films) than they would if the gas were not present and oil was the only displacing fluid. If this were true, each 1% pore volume of gas trapped would cause approximately 0.5% pore volume more water to be retained by the rock. Why the oil does not move into the gas containing pores and displace out the gas and additional water is unknown but may be related to some alteration in the stability of a water-oil interface in a pore throat caused by the presence of gas.

There are many investigators who have found that a trapped gas phase can improve oil recovery by waterflood (Neilson and Flock, 1962) (Shiffman and Breton, 1949) (Holmgren and Morse, 1951) (Bass, 1955) (Kyte et al., 1956) (Dyes, 1954) (Higgins and Leighton, 1962) (Higgins and Leighton, 1967) (Khelil, 1983). According to the results of the three phase capillary pressure measurement presented herein, the gas must be trapped in the oil phase, meaning solution gas, in order to improve S_{or} . Gas trapped in the water did not improve the oil recovery significantly. The difference between the S_w values after primary imbibition for the two phase and three phase curves is again due to the fact that, in the three phase core, water was displacing gas, not oil. But, as would be expected, although the presence of gas may affect the drainage of water by oil, it had little effect on the displacement of oil by water imbibition. After secondary imbibition, the resulting three phase S_w (59%) was close to the 55% value for the two phase core. It is believed that had the gas been trapped by the oil (like gas coming out of solution), the presence of gas might have decreased S_{or} more significantly, as has been observed in the waterflooding of undersaturated reservoirs.

In the tertiary drainage curve, the three phase S_{wi} , was again higher than the two phase S_{wi} , implying the trapped gas remained in the core and had the same effect as in secondary drainage. This fact was backed up by material balance which showed little gas production throughout the experiment.

Overall, the effect of trapped gas on the Oil – Water Capillary pressure curve is shown solely by the increase in irreducible water saturation for both the secondary and tertiary drainages. The influence of the gas invalidates the use of the Hassler and Brunner method for determining the endpoint saturations.

4.3 Gas – Oil Capillary Pressure

Due to the process by which oil and natural gas are trapped and form reservoirs, hydrocarbons are always found in the presence of connate water. Therefore a study of two phase gas – oil capillary pressure without an initial water saturation would not have application to petroleum production. For this reason, only three phase gas – oil capillary pressure measurements were made. The primary, secondary, and tertiary drainage curves for gas and oil in the presence of water are plotted in Figure 13.

At zero capillary pressure, the primary drainage curve shows the initial water saturation was 25%. No gas was present in the core and the oil was drained to a remarkably low 3-4% S_{or} . The similar drainages of oil by gas to establish S_{or} in the three phase gas-water measurements or preceeding the imbibition of oil to establish S_{gr} in the three phase oil-water measurements also resulted in low S_{or} values (8%). It is possible that a small error of a few percent in material balance would account for the exceptionally low S_{or} measured in this case.

Following the primary drainage, oil was imbibed to a low S_{gr} of about 5%. Subsequent secondary and tertiary drainages resulted in a substantially higher S_{or} of nearly 20%. As these curves suggest, the imbibition of oil traps gas bubbles which block the drainage of some oil ganglia and reduce the efficiency of surface film drainage. The significance of this is directly applicable to the gravity drainage process in oil reservoirs. Primary gravity drainage is a more efficient recovery process than secondary drainage. Most reservoirs under gravity drainage, however, are below their bubble point pressure (the cause of the gas cap formation) and the

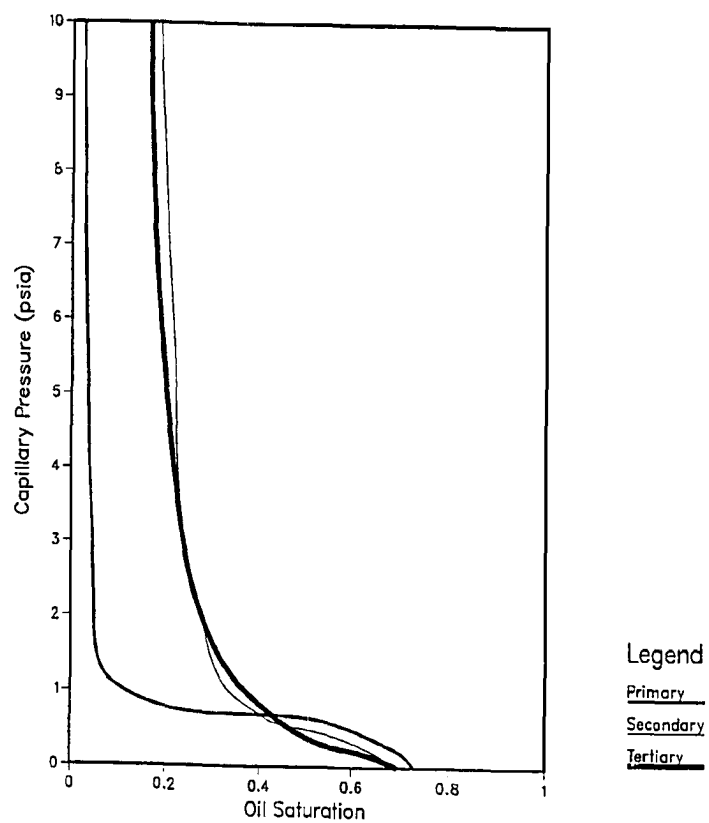


Figure 13. Gas – Oil Capillary Pressure
Three Phase Primary, Secondary, and Tertiary Drainage

drainage of the reservoir oil is comparable to the secondary or tertiary drainages shown in Figure 11. Although a 20% S_{or} is extremely low for reservoir conditions, the primary drainage curve suggests that recovery efficiency could be improved if the displacement was carried out above the bubble point. This could be done by producing saturated reservoirs from the middle or bottom of the oil zone while injecting a non-condensable gas into the top of the formation. Besides the effect of an efficient gravity drainage, there are other advantages gained from maintaining the reservoir pressure. Viscosity reduction and longer primary production without the aid of gas lift or mechanical and electrical pumps are two.

Another application of these results would be in a reservoir undergoing a simultaneous gravity drainage and waterflood. This can be found in some large reservoirs, like Prudhoe Bay, which have an encroaching water aquifer or imposed waterflood at the outer boundaries and produce by gravity drainage in the thicker central portion. In the region where those two recovery mechanisms meet, it is important that the oil bank moving ahead of the water front not be pushed back up into the gas swept zone. This would result in a permanent reduction in recovery as the secondary drainage would not be as efficient as the initial drainage.

The results of the gas – oil capillary pressure measurements concur with other investigators that S_{or} can be very low when drained by gas in the presence of water (Chatzis et al., 1988) (Kantzas et al., 1988). Furthermore, these results show that recovery by gas drainage is optimal under fully saturated conditions.

4.4 Core Cleaning Effectiveness

To enable the use of the same core for both the two phase and three phase experiments, the cores were cleaned by soxlet extraction with toluene for approximately 12 hours. This was followed by a similar extraction with acetone. Then, the cores were heated to 180° F to dry them. It was observed that the acetone changed from colorless to a slight yellowish tint after a long extraction. A sample of the acetone was tested by an infrared spectrophotometer and found to contain an unidentified organic substance. This color change was found after cleaning freshly fired cores as well as the cores already used in the experiments. It was concluded that the organic matter was derived from the inactive clay material in the core. To ensure that this extraction process would not affect the capillary pressure curves or saturation values in any way, complete primary and secondary drainages were carried out using the same core sample and fluids (oil and water). A comparison of both curves revealed no change in the shape or values of the capillary pressure curve due to this stripping of trace amounts of organic matter. It was therefore determined that the cleaning procedure was effective and did not affect the results in any way.

5. Conclusions

Capillary pressure measurements were made of Berea samples containing three phases of fluids by the centrifuge method. Primary, secondary and tertiary drainage capillary pressure curves were constructed for gas and oil in the presence of connate water. Secondary and tertiary curves were constructed for oil and water in the presence of trapped gas, and gas and water in the presence of residual oil. These were compared with secondary and tertiary drainage curves of two phase oil-water and gas-water measurements. The following conclusions can be drawn from the analysis of these curves:

1. The presence of a 20% saturation of gas trapped in the water phase did not significantly affect the residual oil saturation but caused a 12% increase in the irreducible water saturation upon drainage by oil. There was no effect of the trapped gas phase on the shape of the oil-water capillary pressure curve.
2. The effect of a residual oil saturation on gas-water capillary pressure showed that the oil, although trapped in the core, was mobile during the drainage and influenced both the shape of the curve and the resulting irreducible water saturation.
3. Gas displacement of oil in the presence of water results in a very low residual oil saturation (less than 10%). No effect of the presence of water could be determined.
4. The residual oil saturation in a secondary gas displacement in the presence of water is significantly higher than in primary gas displacement.

5. The Hassler – Brunner method for determining end point water saturation values in centrifuge experiments was determined to be invalid for cores containing three phases of fluids. This is because the trapped phase saturation cannot be assumed constant at the core end face throughout the range of capillary pressure applied to generate a typical capillary pressure drainage curve. In other words, the end face saturation of the third phase is unknown, thereby making the estimation of the end point water saturation an indeterminant problem.
6. For sandstone reservoirs containing three phases of fluids, use of conventional two phase capillary pressure measurements may result in an invalid representation of the capillary pressure relationship between the two fluids in the presence of a third phase.

6. Recommendations for Future Work

Based on the results of the present work, further investigation is encouraged in the following areas:

1. effect of mobile saturations on capillary pressures; ie., to determine if the effect of a third phase intensifies or diminishes with increasing third phase saturation.
2. measurement of saturation profiles in cores containing three phases. This could verify the mobilization of the third phase and give insight into the mechanisms of displacement of the residual phase.
3. effect of temperature on the effect of third phase on capillary pressure.

7. Bibliography

Adam, N.K.: *Physics and Chemistry of Surfaces*, Dover Publications, New York (1968).

Adamson, A.W.: *Physical Chemistry of Surfaces, 3rd Edition*, John Wiley and Sons (1976).

Amaefule, J.O., Handy, L.L.: "The Effect of Interfacial Tensions on Relative Oil/Water Permeabilities of Consolidated Porous Media," *Soc. of Pet. Eng. Jour.*, pp. 371 – 381 (June 1982).

Amott, E.: "Observations Relating to the Wettability of Porous Rock," *Trans. AIME*, **216**, pp. 156 – 162 (1959).

Anderson, W. G.: "Wettability Literature Survey—Part 1: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability," *Jour. of Pet. Tech.*, **38**, pp. 1125 – 1144 (October 1986).

Anderson, W.G.: "Wettability Literature Survey—Part 2: Wettability Measurement," *Jour. of Pet. Tech.*, **38**, pp. 1246 – 1262 (November 1986).

Anderson, W.G.: "Wettability Literature Survey—Part 3: The Effects of Wettability on the Electrical Properties of Porous Media," *Jour. of Pet. Tech.*, **38**, pp. 1371 – 1378 (December 1986).

Anderson, W.G.: "Wettability Literature Survey—Part 4: The Effects of Wettability on Capillary Pressure," *Jour. of Pet. Tech.*, **39**, pp. 1283 – 1300 (October 1987).

Barton, C. Longeron, D.G.: "Influence of Very Low Interfacial Tension on Relative Permeability," *Soc. of Pet. Eng. Jour.*, pp. 391 – 401 (October 1980).

Bass, D.M. Jr.: "The Effect on Oil Recovery of Waterflooding at Pressures Above and Below the Bubble Point," M.S. Thesis, Texas A & M University, College Station (Jan. 1955).

Benner, F.C., Bartell, F.E.: "The Effect of Polar Impurities Upon Capillary and Surface Phenomena in Petroleum Production," *Drill. and Prod. Prac.*, pp. 341 – 348 (1941).

Benner, F.C., Dodd, C.G., Bartell, F.E.: "Evaluation of Effective Displacement Pressures of Petroleum Oil-Water Silica Systems," *Drill. and Prod. Prac.*, pp. 169 – 177 (1942).

Bentsen, R.G., Anli, J.: "Using Parameter Estimation Techniques to Convert Centrifuge Data into a Capillary-Pressure Curve," *Soc. of Pet. Eng. Jour.*, pp. 57 – 64 (February 1977).

Bethel, F.T., Calhoun, J.C.: "Capillary Desaturation in Unconsolidated Beds," *Trans. AIME*, **198**, pp. 197 – 202 (1953).

Bobek, J.E., Mattax, C.C., Denekas, M.O.: "Reservoir Rock Wettability—Its Significance and Evaluation," *Trans. AIME*, **213**, pp. 155 – 160 (1958).

Brown, C.E., Neustadter, E.L.: "The Wettability of Oil/Water/Silica Systems with Reference to Oil Recovery," *Jour. of Can. Pet. Tech.*, **19**, no. 3, pp. 100 – 110 (July-September 1980).

Brown, H.W.: "Capillary Pressure Investigations," *Trans. AIME*, **192**, pp. 67 - 74, (1951).

Brown, R.J.S., Fatt, I.: "Measurements of Fractional Wettability of Oilfield Rocks by the Nuclear Magnetic Relaxation Method," *Trans. AIME*, **267**, pp. 262 -264 (1956).

Brown, W.O.: "The Mobility of Connate Water During a Water Flood," *Trans. AIME*, **210**, pp. 190 - 195 (1957).

Bruce, W.A., Welge, H.J.: "Restored State Method for Determination of Oil in Place and Connate Water," API Division of Production, Amarillo Texas, May 22 - 23, 1947.

Buckley, S.E., Leverett, M.C.: "Mechanism of Fluid Displacement in Sands," *Trans. AIME*, **146**, pp. 107 -116 (1943).

Burdine, N.T., Gournay, L.S., Reichertz, P.P.: "Pore Size Distribution of Petroleum Reservoir Rocks," *Trans. AIME*, **189**, pp. 195 - 204 (1950).

Calhoun, J.C. Jr.: "Criteria for Determining Rock Wettability," *Fundamentals of Reservoir Engineering*, No. 442, University of Oklahoma Press, p. 151 (May 1951).

Calhoun, J.C. Jr., Lewis, M. Jr., Newman, R.C.: "Experiments on the Capillary Properties of Porous Solids," *Trans. AIME*, **186**, pp. 189 - 196 (1949).

Carlson, L.O.: "Performance of Hawkins Field Unit Under Gas Drive - Pressure Maintenance Operations and Development of an E.O.R. Project," SPE/DOE

Paper 17324 presented at the 1988 SPE/DOE Symposium on EOR held in Tulsa, OK, April 17 - 20, 1988.

Cardwell Jr., W.T., Parson, R.L.: "Gravity Drainage Theory", *Trans. AIME*, **174**, pp. 199 - 215 (1948).

Chatzis, I., Kantzas, A. Dullien, F.A.L.: "On the Investigation of Gravity-Assisted Inert Gas Injection Using Micromodels, Long Berea Sandstone, and Computer-Assisted Tomography," SPE Paper 18284, SPE Annual Technical Conference and Exhibition, Reservoir Engineering, Oct. 2-5, 1988, pp. 223 - 234.

Chatzis, I., Morrow, N.R.: "Correlation of Capillary Number Relationships for Sandstones," SPE 10114, presented at the SPE Annual Fall Technical Conference and Exhibition, San Antonio, Texas, October 5 - 7, 1981.

Chatzis, I., Morrow, N.R., Lim, H.T.: "Magnitude and Detailed Structure of Residual Oil Saturation," */spej*, pp. 311 - 326 (April 1983).

Chilinger, G.V., Yen, T.F.: "Some Notes On Wettability and Relative Permeabilities of Carbonate Reservoir Rocks, II," *Energy Sources*, **7**, no. 1, pp. 67 - 75 (1983).

Cole, F.C.: *Reservoir Engineering Manual*, Guff Publishing Co., Houston p. 104 - 106 (1961).

Coley, F.H., Marsden, S.S., Calhoun, J.C.: "A Study of the Effect of Wettability on the Behavior of Fluids In Synthetic Porous Media," *Prod. Month.*, pp. 29 - 45 (June 1956).

Collins, R.E: *Flow of Fluids Through Porous Materials*, Reinhold Publishing Corporation, New York (1961).

Craig, F.F., Jr.: *The Reservoir Engineering Aspects of Waterflooding*, SPE Monograph Series, vol. 3, pp. 449 – 460, Dallas (1971).

Denekas, M.O., Mattax C.C., Davis, G.T.: "Effect of Crude Oil Components on Rock Wettability," *Trans. AIME*, **216**, pp. 330 – 333 (1959).

Dombrowski, H.S., Brownell, L.E.: "Residual Equilibrium Saturation Of Porous Media," *Ind. and Eng. Chem.*, **46**, no. 6, pp. 1207 – 1219 (June 1954).

Donaldson, E.C., Thomas, R.D.: "Microscopic Observations of Oil Displacement in Water-Wet and Oil-Wet Systems," SPE Paper 3555 (1971).

Donaldson, E.C., Thomas, R.E., Lorenz, P.D.: "Wettability Determination and Its Effect on Recovery Efficiency," *Soc. Pet. Eng. Jour.*, pp. 13 – 20 (March 1969).

Dougherty, E.L., Sheldon, J.W.: "The Use of Fluid-Fluid Interfaces to Predict the Behavior of Oil Recovery Processes," *Soc. Pet. Eng. Jour.*, **4**, pp. 171 – 182 (1964).

Dullien, F. A. L., *Porous Media: Fluid Transport and Pore Structure*, Academic Press, New York (1979).

Dullien, F.A.L., Lai, F.S.Y., MacDonald, I.F.: "Hydraulic Continuity of Residual Wetting Phase in Porous Media," *Jour. Coll. Int. Sci.* **109**, no.1, p. 201 (1986).

Dumore, J.M., Scholls, R.S.: "Drainage Capillary Pressure Function and the Influence of Connate Water," *Soc Pet Eng. Jour.*, pp. 437 - 444 (October 1974).

Dunning, H.N., Johansen, R.T.: "Measurement of Crude Oil Wetting Tendencies," *The Pet. Eng.*, (July 1958).

Dyes, A.B.: "Production of Water-Driven Reservoirs Below Their Bubble Point," *Jour. of Pet. Tech.*, 6, pp. 31 - 35 (October 1954).

Efros, D.A.: "The Displacement of a Two-Component Mixture when the Viscosity of One of the Fluids Being Displaced is Low," *Soviet Physics, Doklady*, no. 3, p. 727 (1958).

Fatt, I., Klikoff, W.A., Jr.: "Effect of Fractional Wettability on Multiphase Flow Through Porous Media," *Jour. of Pet. Tech.*, 11, pp. 71 - 76 (October 1959).

Fayers, E.J., Sheldon, J.W.: "The Effect of Capillary Pressure and Gravity on Two-Phase Fluid Flow in a Porous Media," *Trans. AIME*, 216, pp. 147 - 155 (1959).

Firoozabadi, A., Soroosh, H., Hasanpour, G.: "Drainage Performance and Capillary Pressure Curves Utilizing a New Centrifuge," SPE Paper 15060, pp. 141 - 144.

Fulcher Jr., R.A., Erickson, T., Stahl, C.D.: "The Effect of the Capillary Number and its Constituents on Two-Phase Relative Permeability Curves," SPE Paper 12170 (1983).

Frauenfeld, T.W.J.: "Author's Reply to Discussion of Effect of an Initial Gas Content on Thermal EOR as Applied to Oil Sands," *Jour. of Pet. Tech.*, **40**, p. 1078 (August 1988).

Frauenfeld, T.W.J., Ridley, R.K., Nguyen, D.M.: "Effect of an Initial Gas Content on Thermal EOR as Applied to Oil Sands," *Jour. of Pet. Tech.*, **40**, pp. 333 - 338 (March 1988).

Gatenby, W.A., Marsden, S.S.: "Some Wettability Characteristics of Synthetic Porous Media," *Prod. Month.*, pp. 9 -12 (November 1957).

Gardner, G.H.T., Messmer, J.H., Woodside, W.: "Effective Porosity and Gas Relative Permeability," Conference on Theory of Fluid Flow in Porous Media, School of Petroleum Engineering, Univ. of Oklahoma, p. 171 (March 22 - 23, 1959).

Geffen, T.M., Parrish, D.R., Haynes, G.W.: "Efficiency of Gas Displacement From Porous Media By Liquid Flooding," *Trans. AIME*, **195**, pp. 29 - 38 (1952).

Gibbs, J. W.: *Scientific Papers*, Dover Publications, New York, pp. 242 - 252 (1961).

Goddard, R.R., Gardner, G.H.F., Wyllie, M.R.J.: "Some Aspects of Multi-Phase Distribution in Porous Bodies," *Interaction Between Fluids and Particles*, London Inst. of Chem. Engrs., pp. 326 - 332 (1962).

Gorring, R.L.: "Multiphase Flow of Immiscible Fluids in a Porous Media," Ph.D. dissertation, University of Michigan (1978).

Hacket, F.E., Strellan, J.S.: "The Capillary Pull of an Ideal Soil," *J. Agr. Sci.*, **10**, p. 671 (1928).

Hagoort, J.: "Oil Recovery by Gravity Drainage," *Soc. of Pet. Eng. Jour.*, pp. 139 - 150 (June 1980).

Haines, W.B.: "Studies in the Physical Property of Soil, IV. A Further Contribution to the Theory of Capillary Phenomena in Soils," *J. Agri. Sci.*, vol **17**, p. 264 (1927).

Haines, W.B.: "Studies in the Physical Property of Soil, V. The Hysteresis Effect in Capillary Properties and The Modes of Moisture Distribution Associated Therewith," *J. Agri. Sci.*, v. **20**, p. 97 (1930).

Handy, L.L.: "Determination of Effective Capillary Pressures for Porous Media from Imbibition Data," *Trans. AIME*, **219**, pp. 75 - 80 (1960).

Handy, L.L., Datta, P.: "Fluid Distribution During Immiscible Displacements in Porous Media," *Soc. of Pet. Eng. Jour.*, pp. 261 - 266 (September 1960).

Harbert, L.W.: "Low Interfacial Tension Relative Permeability," SPE 12171, presented at the Annual Technical Conference and Exhibition, San Francisco, California (October 5 - 8, 1983).

Harris, C.C., Jowett, A. Morrow, N.R.: "Effect of Contact Angle on the Capillary Properties of Porous Masses," *Trans. Inst. of Mining and Metal.*, v. **73**, no. 5, pp. 335 - 351 (1963-64).

Hassler, G.L., Brunner, E.: "Measuring Capillary Pressure on Small Core Samples," *Trans. AIME*, **160**, pp. 114 – 123 (1945).

Hassler, G.L., Brunner, E., Deahl, T.J.: "The Role of Capillarity in Oil Production," *Trans. AIME*, **155**, pp. 155 – 174 (1944).

Hassler, G.L., Rice, R.R., Leeman, E.H.: "Investigations on the Recovery of Oil from Sandstones by Gas Drive," *Trans. AIME*, **118**, pp. 116 – 137 (1936).

Heibea, A.A., Davis, H.T. Scriven, L.E. : "Effect of Wettability on Two-Phase Relative Permeabilities and Capillary Pressures," SPE Paper 12172 (1983).

Higgins, R.V., Leighton, A.J.: "Computer Prediction of Water Drive of Oil and Gas Mixture Through Irregularly Bounded Porous Media—Three Phase Flow," *Jour. of Pet. Tech.*, **14**, pp. 1048 – 1054 (September 1962).

Higgins, R.V., Leighton, A.J.: "Computer Techniques for Predicting Three Phase Flow in Five Spot Waterfloods," RI7011, USBM (Aug. 1967).

Hoffman, R.N. "A Technique for the Determination of Capillary Pressure Curves Using A Constantly Accelerated Centrifuge," *SPE*, pp. 227 – 235 (September 1963).

Holbrook, O.C., Bernard, G.G.: "Determination of Wettability by Dye Adsorption," *Trans. AIME*, **213**, pp. 261 – 264 (1958).

Holmgren, C.R., Morse, R.A.: "Effect of Free Gas Saturation on Oil Recovery by Water Flooding," *Trans. AIME*, **192**, pp. 135 – 140 (1951).

Hovanessian, S.A., Fayers, F.J.: "Linear Water Flood with Gravity and Capillary Effects," *Soc. of Pet. Eng. Jour.*, pp. 32 -36 (March 1961).

Iwankow, E.N.: "A Correlation of Interstitial Water Saturation and Heterogeneous Wettability," *Prod. Month.*, pp. 18 - 26 (October 1960).

Jennings, H.Y., Jr.: "Surface Properties of Natural and Synthetic Porous Media," *Prod. Month.*, pp. 20 - 23 (March 1957).

Johansen, R.T., Dunning, H.N.: "Relative Wetting Tendencies of Crude Oils by the Capillarimetric Method," *Prod. Month.*, pp. 20 - 22 (September 1959).

Jones-Parra, J. "Comments on Capillary Equilibrium," *Trans. AIME*, **198**, pp. 314 - 316 (1953).

Kantzas, A., Chatzis, I., Dullien, F.A.L.: "Enhanced Oil Recovery by Inert Gas Injection," SPE/DOE Paper 17379, (1988).

Kennedy, H.T., Guerrero, E.T.: "The Effect of Surface and Interfacial Tensions on the Recovery of Oil by Water Flooding," *Trans. AIME*, **201**, pp. 124 - 131 (1954).

Khelil, Chakib: "A Correlation of Optimum Free Gas Saturation with Rock and Fluid Properties", SPE Paper (1983).

Killins, C.R., Nielsen, R.F., Calhoun, J.C.: "Capillary Desaturation and Imbibition in Porous Rocks," *Prod. Month.*, pp. 30 - 39 (December 1953).

Kinney, P.T., Nielsen, R.F.: "Wettability in Oil Recovery," *World Oil*, pp. 145 - 154 (March 1951).

Kyte, J.R., Stanclift, R.J. Jr., Stephan, S.C, Rapoport, L.A. "Mechanism of Water Flooding in the Presence of Free Gas," *Trans. AIME*, 207, pp. 215 - 221 (1956).

Lebastie, A., Guy, M., Delclaud, J.P., Iffly, R.: "Effect of Flow Rate and Wettability on Water-Oil Relative Permeabilities and Capillary Pressure," SPE Paper 9236 (1980).

Latil, M.: *Enhanced Oil Recovery*, Editions Techniq, Paris (1980).

Lefebvre du Prey, E.J.: "Factors Affecting Liquid-Liquid Relative Permeabilities of a Consolidated Porous Medium," *SPEJ* pp. 39 - 47 (February 1973).

Leverett, M.C.: "Capillary Behavior in Porous Solids," *Trans. AIME*, 142, pp. 152 - 169 (1941).

Lorenz, P.B., Donaldson, E.C., Thomas, R.D.: "Use of Centrifugal Measurements of Wettability to Predict Oil Recovery," Report of Investigation 7873, United States Bureau of Mines (1974).

Marsden, S.S.: "Wettability: The Elusive Key to Water Flooding," *Petroleum Engineer*, pp. 82 - 87 (April 1965).

Marx, J.W.: "Determining Gravity Drainage Characteristics on the Centrifuge," *Trans. AIME*, 207, pp. 88 - 91 (1956).

McCaffery, F.G.: "The Effect of Wettability on Relative Permeability and Imbibition in Porous Media," Ph.D. dissertation, University of Calgary (1973).

McCullough, J.J., Albaugh, F.W., Jones, P.H.: "Determination of the Interstitial-Water Content of Oil and Gas Sand by Laboratory Tests of Core Samples," *Drill. and Prod. Prac.*, pp. 180 - 187 (1944).

McGhee, J.W., Crocker, M.E., Donaldson, E.C.: "Relative Wetting Properties of Crude Oils in Berea Sandstone," U.S. Department of Energy, BETC/R1-78/9, (January, 1979).

Melrose, J.C.: "Interfacial Phenomena as Related to Oil Recovery Mechanisms," *The Can. Jour. of Chem. Eng.*, 48 pp. 638 - 643 (December 1970).

Melrose, J.C.: "Wettability as Related to Capillary Action in Porous Media," *Soc. of Pet. Eng. Jour.*, pp. 259 - 271 (September 1965).

Melrose, J.C.: "Interpretation of Centrifuge Capillary Pressure Data," *The Log Analyst*, pp 40 - 47 (January-February 1988).

Melrose, J.C., Brandner, C.F.: "Role of Capillary Forces in Determining Microscopic Displacement Efficiency for Oil Recovery by Waterflooding," *Jour. of Can. Pet. Tech.*, 13, no. 54 (1974).

Moore, T.F., Slobod, R.L.: "The Effect of Viscosity and Capillarity On the Displacement of Oil by Water," *Prod. Month.*, pp. 20 - 25 (August 1956).

Morrow, N.R.: "Capillary Pressure Correlations for Uniformly Wetted Porous Media," *Jour. of Can. Pet. Tech.*, **15**, no. 4, pp. 49 – 69 (October-December 1976).

Morrow, N.R.: "Irreducible Wetting Phase Saturation in Porous Sedimentary Rocks," *AAPG Bull.*, **55**, no. 3, pp. 514 – 522 (March 1971).

Morrow, N.R.: "Physics and Thermodynamics of Capillary," *Indus. and Eng. Chem.*, **62**, no. 5, pp. 32 – 56 (June 1970).

Morrow, N.R., Lim, H.T., Ward, J.S.: "Effect of Crude-Oil-Induced Wettability Changes on Oil Recovery," *SPE Formation Evaluation*, pp. 89 – 103 (February 1986).

Morrow, N.R., Mungan, N.: "Wettability and Capillarity in Porous Media," Petroleum Recovery Institute research report RR-7 (January 1971).

Morrow, N.R., Songkran, B.: "Effect of Viscous and Bouyancy Force on Non-wetting Phase Trapping in Porous Media," *Surface Phenomena in Enhanced Oil Recovery*, ed. D. O. Shah, Plenum Press, NY (1981).

Mungan, N.: "Certain Wettability Effects In Laboratory Waterfloods," *Jour. of Pet. Tech.*, **237**, pp. 247 – 252 (February 1966).

Mungan, N.: "Enhanced Oil Recovery Using Water as a Driving Fluid: Part II – Interfacial Phenomena and Oil Recovery: Wettability," *World Oil*, pp. 77 – 83 (March 1981).

Mungan, N.: "Enhanced Oil Recovery Using Water as a Driving Fluid: Part III - Interfacial Phenomena and Oil Recovery: Capillarity," *World Oil*, pp. 149 - 158 (May 1981).

Mungan, N.: "Interfacial Effects in Immiscible Liquid-Liquid Displacement in Porous Media," *Soc. of Pet. Eng. Jour.*, pp. 247 - 253 (September 1966).

Mungan, N.: "Role of Wettability and Interfacial Tension in Water Flooding," *Soc. of Pet. Eng. Jour.*, pp. 115 - 123 (June 1964).

Muskat, M: *Flow of Homogeneous Fluids Through Porous Media*, McGraw Hill Book Co. Inc., New York (1961).

Muskat, M.: *Physical Principles of Oil Production*, McGraw-Hill Book Co. Inc., New York, New York (1959).

Neilson, I.D.R., Flock, D.L.: "The Effect of a Free Gas Saturation on the Sweep Efficiency of an Isolated Five Spot," *Can. Mining and Metal. Bul.*, **55**, no. 598, pp. 124 - 129 (February 1962).

O'Meara, D.J., Hirasaki, G.J., Rohan, J.A.: "Centrifuge Movements of Capillary Pressure: Part 1—Outflow Boundary Condition," SPE Paper 18296, SPE Annual Technical Conference and Exhibition, Reservoir Engineering, pp. 349 - 362 (October 2-5, 1988).

Omeregic, Z.S.: "Factors Affecting the Equivalency of Different Capillary Pressure Measurement Techniques," SPE Paper 15384 (1986).

Perkins, F.M., Jr.: "An Investigation of the Role of Capillary Forces in Laboratory Water Floods," *Trans. AIME*, **210**, pp. 199 – 201 (1957).

Pickell, J.J., Swanson, B.F., Hickman, W.B.: "Application of Air-Mercury and Oil-Air Capillary Pressure Data in the Study of Pore Structure and Fluid Distribution," *Soc. of Pet. Eng. Jour.*, pp. 55 – 61 (March 1966).

Pirson, S.J.: *Oil Reservoir Engineering*, McGraw-Hill Book Company Inc., New York (1958).

Plateau, "Statique expérimentale et théorique des Liquides soumis aux seules Forces moléculaires" (1873).

Purcell, W.R.: "Capillary Pressures—Their Measurement Using Mercury and the Calculation of Permeability Therefrom," *Trans. AIME*, **186**, pp. 39 – 48 (1949).

Purcell, W.R.: "Interpretation of Capillary Pressure Data," *Trans. AIME*, **189**, pp. 369 – 371 (1950).

Raimondi, P.: "Distribution of the Oil Phase Obtained Upon Imbibition of Water," *Soc. of Pet. Eng. Jour.*, **231**, pp. 49 – 55 (March 1964).

Rathmall, J.J., Braun, P.H., Perkins, T.K.: "Reservoir Waterflood Residual Oil Saturation from Laboratory Tests," *Jour. of Pet. Tech.*, **255** pp. 175 – 185 (February 1973).

Raza, S.H., Treiber, L.E., Archer, D.L.: "Wettability of Reservoir Rocks and Its Evaluation," *Prod. Month.*, pp. 2 – 7 (April 1968).

Reisberg, J., Doscher, T.M.: Interfacial Phenomena in Crude-Oil-Water Systems," *Prod. Month.*, pp. 43 – 50 (November 1956).

Richardson, J.G.: "Flow Through Porous Media," *Handbook of Fluid Dynamics*, Section 16, McGraw-Hill, New York (1961).

Rose, W., Bruce, W.A.: "Evaluation of Capillary Character in Petroleum Reservoir Rock," *Trans. AIME*, **186**, pp. 127 – 142 (1949).

Rosman, A., Simon, A.: "Flow Heterogeneity in Reservoir Rocks," *Jour. of Pet. Tech.*, **28**, pp. 1427 – 1429 (December 1976).

Salathiel, R.A.: "Oil Recovery by Surface Film Drainage in Mixed Wettability Rocks," *Jour. of Pet. Tech.*, **255**, pp. 1216 – 1224 (October 1973).

Schechter, R.S., Lam, C.S., Wade, W.H.: "Mobilization of Residual Oil Under Equilibrium and Nonequilibrium Conditions," SPE 10198, presented at Annual Fall Technical Conference and Exhibition, San Antonio, Texas (October 5 -7 1981).

Schenk, L.: "Discussion of Effect of an Initial Gas Content on Thermal EOR as Applied to Oil Sands," *Jour. of Pet. Tech.*, **40**, p 1077 (May 1988).

Shiffman, L., Breston, J.N.: "The Effect of Gas on Recovery When Water-flooding Long Cores," Paper 54, Penn State College Mineral Industries Experiment Station (October 1949).

Sheffield, M.: "Three-Phase Fluid Flow Including Gravitational, Viscous, and Capillary Forces," *Soc. of Pet. Eng. Jour.*, **9**, pp. 225 – 269 (1969).

Sinnokrot, A.A., Ramey, Jr., M.J., Marsden, S.S.: "Effect of Temperature Level Upon Capillary Pressure Curves," *Soc. of Pet. Eng. Jour.*, pp. 13 - 22 (March 1971).

Skuse, B., "Capillary Pressure Measurements in Reservoir Rock Cores Using the Centrifuge," Beckman Instruments, Inc., publication DS-607.

Skuse, B., Firoozabadi, A., Ramey, H.J., Jr.: "Computation and Interpretation of Capillary Pressure from a Centrifuge," SPE Paper 18297, SPE Annual Technical Conference and Exhibition, Reservoir Engineering, October 2-5 1988, pp. 363 - 372.

Slobod, R.L., Chambers, A., Prehn, W.L., Jr.: "Use of Centrifuge for Determining Connate Water, Residual Oil, and Capillary Pressure Curves of Small Core Samples," *Trans. AIME*, **192**, pp. 127 - 134 (1951).

Smith, W.O., Foote, P.D., Busang, P.F.: "Capillary Rise in Sands in Uniform Spherical Grains," *Physics* **1** p. 18 (1931).

Smith, W.O.: "Minimum Capillary Rise in an Ideal Uniform Soil," *Physics*, **4**, p. 184 (1933).

Soo, H., Radke, C.J.: "Pore-Size Distributions from the Centrifuge Technique," *Soc. of Pet. Eng. Jour.*, pp. 1 - 31 (July 1983).

Stahl, C.D., Nielsen, R.F.: "Residual Water and Residual Oil By Capillary Pressure Techniques," *Prod. Month.*, pp. 19 - 22 (January 1950).

Taber, J.J.: "Dynamic and Static Forces Required to Remove a Discontinuous Oil Phase From Porous Media Containing Both Oil and Water," *Soc. of Pet. Eng. Jour.*, pp. 3 - 12 (March 1969).

Thomeer, J.H.M.: "Introduction of a Pore Geometrical Factor Defined by the Capillary Pressure Curve," *Trans. AIME*, **219**, pp. 354 - 358 (1960).

Thornton, O.F., Marshall, D.L.: "Estimating Interstitial Water by the Capillary Pressure Method," *Trans. AIME*, **170**, pp. 69 - 80 (1947).

Tiffin, D.L. Yellig, W.F.: "Effects of Mobile Water on Multiple-Contact Miscible Gas Displacement," *Soc. of Pet. Eng. Jour.*, pp. 447 - 455 (June 1983).

von Englehardt, W.: "Interstitial Water of Oil Bearing Sands in Porous Sandstones," *Proc. Fourth World Petroleum Conference, Rome, Sec. 1/C*, pp. 399 - 416 (June 6 - 15, 1955).

Wagner, O.R., Leach, R.O.: "Effect of Interfacial Tension on Displacement Efficiency," *Soc. of Pet. Eng. Jour.*, pp. 335 - 344 (1966).

Welge, H.J.: "Displacement of Oil from Porous Media by Water or Gas," *Trans. AIME*, **179** pp. 133 - 145 (1949).

Willhite, G.P.: *Waterflooding*, Society of Petroleum Engineers, Richardson, Texas (1986).

Wunderlich, R.W.: "Imaging of Wetting and Nonwetting Phase Distributions: Application to Centrifuge Capillary Pressure Measurements," *SPE Paper 14422* (1985).

Wyckoff, R.D., Botset, H.G.: *Physics*, **7**, 325 (1936).

Yuster, S.T., Stahl, C.D.: "Capillary Pressure Studies," *Prod. Month.*, **24**
(December 1984).

Appendix: Centrifuge Data

Table A.1. Two Phase Gas – Water Drainage Centrifuge Data

<u>Secondary Drainage</u>		<u>Tertiary Drainage</u>	
$\underline{P_c}$	$\underline{\bar{S}_w}$	$\underline{P_c}$	$\underline{\bar{S}_w}$
0.000	0.749	0.000	0.750
0.664	0.749	0.664	0.750
0.992	0.732	0.992	0.733
1.472	0.723	1.472	0.724
2.259	0.688	2.259	0.680
3.279	0.605	3.279	0.597
5.289	0.518	5.289	0.488
8.820	0.430	8.820	0.392
11.714	0.387	11.714	0.366

Table A.2. Three Phase Gas – Water Drainage Centrifuge Data

<u>Secondary Drainage</u>		<u>Tertiary Drainage</u>	
$\underline{P_c}$	$\underline{\bar{S}_w}$	$\underline{P_c}$	$\underline{\bar{S}_w}$
0.000	0.775	0.000	0.802
0.992	0.766	0.820	0.802
1.470	0.739	1.181	0.793
2.260	0.623	2.259	0.672
3.280	0.538	3.755	0.547
5.290	0.426	5.289	0.484
8.820	0.336	7.477	0.434
11.714	0.287	10.043	0.390

Table A.3. Two Phase Oil - Water Drainage Centrifuge Data

<u>Secondary Drainage</u>		<u>Tertiary Drainage</u>	
$\underline{P_c}$	$\underline{\bar{S}_w}$	$\underline{P_c}$	$\underline{\bar{S}_w}$
0.000	0.548	0.000	0.467
0.196	0.548	0.196	0.467
0.800	0.425	0.800	0.305
1.495	0.346	1.495	0.248
2.504	0.294	2.504	0.191
3.950	0.250	3.950	0.156
6.995	0.206	6.995	0.116
10.015	0.171	10.015	0.081

Table A.4. Three Phase Oil - Water Drainage Centrifuge Data

<u>Secondary Drainage</u>		<u>Tertiary Drainage</u>	
$\underline{P_c}$	$\underline{\bar{S}_w}$	$\underline{P_c}$	$\underline{\bar{S}_w}$
0.000	0.686	0.000	0.604
0.196	0.686	0.196	0.604
0.800	0.637	0.800	0.468
1.495	0.538	1.495	0.437
2.504	0.467	2.504	0.381
3.950	0.413	3.950	0.336
6.995	0.341	6.995	0.293
10.015	0.314	10.015	0.271

Table A.5. Three Phase Gas - Oil Drainage Centrifuge Data

<u>Primary Drainage</u>		<u>Secondary Drainage</u>		<u>Tertiary Drainage</u>	
$\underline{P_c}$	$\underline{\bar{S}_o}$	$\underline{P_c}$	$\underline{\bar{S}_o}$	$\underline{P_c}$	$\underline{\bar{S}_o}$
0.000	0.724	0.000	0.063	0.000	0.695
0.575	0.724	0.575	0.603	0.575	0.695
0.796	0.628	0.796	0.511	0.796	0.599
1.995	0.305	1.995	0.331	1.995	0.415
3.001	0.213	3.001	0.272	3.001	0.356
6.019	0.125	6.019	0.197	6.019	0.285
10.031	0.088	10.031	0.168	10.031	0.243